Application of Enriched Stable Mercury Isotopes to the Lake 658 Watershed for the METAALICUS Project, at the Experimental Lakes Area, Northwestern Ontario, Canada

Ken A. Sandilands[1], John W.M. Rudd[2], Carol A. Kelly[2], Holger Hintelmann[3], Cynthia C. Gilmour[4], and Michael T. Tate[5,6]

[1]Central and Arctic Region
Fisheries and Oceans Canada
Winnipeg, MB R3T 2N6

[2]R & K Research
Salt Spring Island, BC
V8K 2J3

[3]Trent University
Peterborough, ON K9J 7B8

[4]Smithsonian Environmental Research Center
Edgewater, MD 21037

[5]US Geological Survey
Middleton, WI 53562

[6]University of Wisconsin
Madison, WI 53706

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Fisheries and Oceans Canada
Freshwater Institute
501 University Crescent
Winnipeg, MB
R3T 2N6
E-mail: sandilandsk@dfo-mpo.gc.ca

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ABSTRACT

Sandilands, K.A., J.W.M. Rudd, C.A. Kelly, H. Hintelmann, C.C. Gilmour, and M.T. Tate. 2005. Application of enriched stable mercury isotopes to the Lake 658 watershed for the METAALICUS project, at the Experimental Lakes Area, northwestern Ontario, Canada. Can. Tech. Rep. Fish. Aquat. Sci. 2597: viii + 48 p.

Since 2000 the Lake 658 watershed at the Experimental Lakes Area in northwestern Ontario has been the site of a whole-ecosystem experiment designed to study the relationship between atmospheric deposition of mercury and mercury accumulation in fish, as well as the biogeochemical processing of mercury within watersheds. The experiment is termed METAALICUS, - Mercury Experiment To Assess Atmospheric Loading in Canada and the United States. Atmospheric loadings of mercury to the watershed were increased to 4 times the rate normally occurring in wet deposition in the region using enriched stable isotopes of mercury. Loadings to the uplands and wetland in the watershed were done via aircraft, whereas loadings to the lake were done by injection into the epilimnion from a boat. This report describes the Lake 658 watershed, application techniques, and estimations of application rates. From 2001-2003, total mercury loadings to the upland, wetland, and lake were 62, 78 and 66 $\mu g/m^2$ respectively.

KEY WORDS: Mercury, METAALICUS, ELA, Atmospheric Loading

RÉSUMÉ

Sandilands, K.A., J.W.M. Rudd, C.A. Kelly, H. Hintelmann, C.C. Gilmour, and M.T. Tate. 2005. Application of enriched stable mercury isotopes to the Lake 658 watershed for the METAALICUS project, at the Experimental Lakes Area, northwestern Ontario, Canada. Can. Tech. Rep. Fish. Aquat. Sci. 2597: viii + 48 p.

Depuis 2000, le bassin du lac 658 de la région des lacs expérimentaux du Nord-Ouest de l'Ontario est le site d'une expérience panécosystémique, appelée METAALICUS (pour Mercury Experiment to Assess Atmospheric Loading in Canada and the United States), ayant pour objet d'étudier le lien entre la charge atmosphérique de mercure et l'accumulation de mercure dans le poisson ainsi que le cycle biogéochimique du mercure dans les bassins hydrographiques. Les retombées de mercure sur le bassin ont été augmentées à quatre fois la valeur des dépôts humides naturels par un apport d'isotopes enrichis stables de mercure. Le mercure a été dispersé par avion au-dessus des milieux secs et des milieux humides et injecté dans l'épilimnion du lac. Le présent rapport décrit le bassin du lac 658 et les procédés d'application de mercure et donne les estimations relatives à la charge de mercure. De 2001 à 2003, la charge totale de mercure qui est entrée dans les milieux secs, les milieux humides et le lac était respectivement de 62, 78 et 66 $\mu g/m^2$.

MOTS-CLÉS: Mercury, METAALICUS, ELA, Atmospheric Loading

INTRODUCTION

The **M**ercury **E**xperiment **T**o **A**ssess **A**tmospheric **L**oading **I**n **C**anada and the **U**nited **S**tates (METAALICUS) is a whole ecosystem manipulation experiment that began in 1999 at the Experimental Lakes Area (ELA), northwestern Ontario, Canada. The objectives of METAALICUS are to determine: 1) the relationship between atmospheric mercury (Hg) loading and Hg concentrations in fish and other biota, 2) the relative importance of newly deposited Hg onto wetlands, uplands, and the lake surface as sources of mercury to fish and other biota, 3) how quickly Hg concentrations in the lake, upland, and wetland respond to changes in Hg deposition rate, and 4) the relative importance of newly deposited Hg as compared to Hg present in the ecosystem from previous years.

The overall design of the experiment was to load a watershed with an amount of Hg (25 $\mu g/m^2/yr$) equivalent to approximately four times the normal rate of wet ambient Hg deposition (6-7 $\mu g/m^2/yr$, St. Louis et al. 2001). To distinguish the relative importance of Hg deposition in different areas of the watershed to fish Hg concentrations, the uplands, wetlands, and the lake, were sprayed with different stable isotopes of mercury, ^{200}Hg, ^{198}Hg, ^{202}Hg respectively.

This report describes methods used to apply Hg onto the watershed, and estimates application rates and spray drifts to various parts of the watershed.

SITE DESCRIPTION

The experiment was carried out in the Lake 658 basin of the ELA (Figure 1). A topographical map of the lake and its watershed is shown in Figure 2, and the surface areas of the components of this watershed are given in Table 1.

Table 1. Areas of each component of the Lake 658 basin, and isotopes applied to each area.

	Area (ha)	Isotope Applied
Uplands	42.09	^{200}Hg
Wetland	1.66	^{198}Hg
Lake	8.39	^{202}Hg

The Lake 658 basin is located at 49^0 43.95' N latitude and 93^0 44.2' W longitude. Lake 658 is a small, oligotrophic, headwater lake which receives water through direct deposition, one gauged upland stream inflow, direct runoff, sub-surface flow, and partially gauged inflow from the adjacent wetland (Figure 2). The wetland drains via a stream entering the lake near the south west corner, and also by sub-surface flow through the peat. Discharges from the upland and wetland streams into the lake are measured by flumes operated by the United States Geological Survey (USGS, see Figure 2). The outflow at the north east end of the lake flows into Winnange lake most of the time. However after large rain events the level of Winnange may become higher and the flow is reversed.

The long term average water residence time of Lake 658, estimated from watershed area (52 ha), lake volume (547,966 m^3), average annual precipitation

(700 mm), and water yield (31%), is approximately 5.5 years (K. G. Beaty, pers. comm.), but can vary greatly between years. Lake 658 is a double basin lake. The northeast basin has a maximum depth of 11 m and the southwest basin 13 m. The mean depth of the lake as a whole is 6.55 m (Figure 3). Maximum fetch is 615 m and the surface area is 8.39 ha. The lake is dimictic with the whole water column circulating in spring and fall. Ice cover is an average of six months/year.

The Upland (defined as any area with higher elevation than the shoreline or wetland) has mixed forest vegetation. There is a small area in the upper northwest corner of the watershed that was previously logged around 1978 (Figure 4) and is dominated by deciduous tree species, predominantly red maple (*Acer rubrum* L.) and white birch (*Betula papyrifera* Marsh.). Most of the watershed located south of the lake, and small portions north of the lake were burned in the fall of 1983 (Figure 4) resulting in dense stands of jack pine (*Pinus banksiana* Lamb.) interspersed with some birch. Much of the watershed north of the lake was not burned and supports mature old growth trees dominated by, balsam fir (*Abies balsamea* (L.) Mill.), black spruce (*Picea mariana* (Mill.) BSP.), poplar (*Populus spp.*) and jack pine forest. Upland ground vegetation communities are shade-tolerant and include juniper (*Juniperus communis* L.) and blueberry (*Vaccinium angustifolium* Ait.), shrubs, mosses and lichens.

Most of the wetland supports sparse stands of jack pine, black spruce, tamarack (*Larix laricina* (Du Roi) K. Koch) and alder *(Alnus rugosa* (Du Roi) Spreng.). A small band directly adjacent to the lake supports emergent vegetation growth. Wetland ground vegetation is comprised predominantly of moss (*Sphagnum* spp.) and some Labrador tea (*Ledum groenlandicum* Oeder) and club mosses (*Polypodium* spp).

METHODS

Definition of Terms

Hg solutions applied in this experiment were not pure solutions of a specific isotope, the solutions were enriched to varying degrees with the appropriate isotope. Therefore, in this report, the term *Spike Hg* is defined as the total amount of inorganic Hg(II) applied or measured subsequently in samples. For example, the Hg solution applied to the upland was enriched with ^{200}Hg (80.45%) and the remaining 19.55% were other Hg isotopes. Therefore, the amount of *Upland Spike Hg* applied is the amount of ^{200}Hg applied divided by 0.8045. For environmental samples, such as lake water, the amount of *Upland Spike Hg* is the amount of ^{200}Hg measured in the sample and calculated to be in excess of the ambient ^{200}Hg, divided by 0.8045. *Ambient Hg* refers to Hg that is deposited under normal circumstances to the watershed. The terms *Wetland Spike Hg* and *Lake Spike Hg* are used in the same way.

The *application rate* ($\mu g Hg/m^2/yr$) is defined as the amount of Hg that was *delivered* from the spray boom of the aircraft to the upland and wetland, or from the peristaltic pump to the lake. In the case of aerial application, there were some losses of isotope to the airplane equipment during application, which

makes the application rate smaller than the target rate. In the case of lake application, there were no similar losses.

The amounts of Hg delivered from the aircraft (the aerial application rates) are maximum amounts that could have actually reached the forest canopy and ground surface vegetation. This is because some Hg probably drifted out of the watershed area or onto the lake surface during application. The amount of this drift was estimated from measurements of terrestrial isotopes in the lake water, or in surface collectors, following aerial applications.

Preparation of Isotope solutions

Enriched stable Hg isotopes (^{198}Hg, ^{200}Hg and ^{202}Hg) were purchased from Trace Sciences International in Richmond Hill, Ontario, Canada. The isotopes were produced by the Kurchatov Institute laboratory in Moscow, Russia.

The Hg was received as mercuric chloride ($HgCl_2$), at the Freshwater Institute, Winnipeg. Spike Hg solutions were made up by diluting with 5% nitric acid, volumes ranging from 100 to 700 mL, and concentrations of 1 to 33 gHg/L. These initial isotope solutions were diluted further before using in spray applications or before adding to the lake. Isotope solubilization and preparation was done at the Freshwater Institute (FWI) Chemistry Lab. Calculations for the isotope preparations were done each year, according to the amounts applied on each area the previous year.

The isotope ratios received from Trace Sciences in 2000 and 2001 were very similar (Tables 2, 3 & 4). In 2003, though, the ^{202}Hg and ^{200}Hg isotopes were more highly enriched than in the previous years. Therefore, the isotopic composition of these two solutions were adjusted so that the enrichment of each isotope solution was similar to previous years' solutions. This adjustment was made by blending the isotopes received from Trace with small amounts of other isotopic solutions and a natural Hg solution.

Table 2. Percent of isotopic enrichment of Upland Spike Hg solutions.

	^{196}Hg	^{198}Hg	^{199}Hg	^{200}Hg	^{201}Hg	^{202}Hg	^{204}Hg
2001	0.09	3.9	3.62	***80.45***	4.01	6.31	1.62
2002	0.09	3.9	3.62	***80.45***	4.01	6.31	1.62
2003 (blend)*	0.11	3.06	3.80	***80.44***	3.54	7.49	1.55

*isotope solutions were blended to make the mixture as similar as possible to composition of isotope solutions used in 2001 and 2002. The number of figures presented here are the same as reported originally by Trace.

Table 3. Percent of isotopic enrichment of Wetland Spike Hg solutions.

	^{196}Hg	^{198}Hg	^{199}Hg	^{200}Hg	^{201}Hg	^{202}Hg	^{204}Hg
2001	0.2	***90.5***	0.8	4.0	2.7	1.5	0.3
2002 and 2003 mixed*	0.23	***90.67***	0.72	3.18	3.55	1.33	0.31

*isotope solutions from 2002 and 2003 were mixed and applied together in 2003 since we were unable to spray the wetland in 2002. The number of figures presented here are the same as reported originally by Trace.

Table 4. Percent of isotopic enrichment of Lake Spike Hg solutions.

	^{196}Hg	^{198}Hg	^{199}Hg	^{200}Hg	^{201}Hg	^{202}Hg	^{204}Hg
2001	0.05	0.70	1.5	4.35	1.65	***90.9***	0.85
2002	<0.10	0.70	1.5	4.3	1.70	***90.8***	0.90
2003 (blend)*	0.06	0.96	1.75	4.28	1.33	***90.81***	0.76

*isotope solutions were blended to make the mixture as similar as possible to composition of isotope solutions used in 2001 and 2002. The number of figures presented here are the same as reported originally by Trace.

The percent of each enriched isotope in the tables above are the guaranteed ratios provided by Trace Sciences. Also, each year, sub-samples of the mercury isotope solutions made up from the isotopes received from Trace Sciences were sent to Holger Hintelmann (Trent University) for verification. The results of these analyses did not differ significantly from the information provided by Trace Sciences (Tables 5, 6 and 7.).

Table 5. Percent of isotopic enrichment of Upland Spike Hg solutions as measured by Hintelmann lab.

	^{196}Hg	^{198}Hg	^{199}Hg	^{200}Hg	^{201}Hg	^{202}Hg	^{204}Hg
2001	0.08	4.04	3.79	***79.52***	4.22	6.63	1.72
2002	0.07	3.64	3.28	***79.66***	3.82	8.08	1.45
2003	0.09	3.06	3.74	***80.61***	3.48	7.42	1.60

Table 6. Percent of isotopic enrichment of Wetland Spike Hg solutions as measured by Hintelmann lab.

	^{196}Hg	^{198}Hg	^{199}Hg	^{200}Hg	^{201}Hg	^{202}Hg	^{204}Hg
2001	0.16	***88.98***	1.09	4.25	2.83	2.26	0.43
2002	0.16	***89.18***	1.05	4.26	2.85	2.06	0.44
2003	0.20	***89.61***	0.91	3.43	3.66	1.79	0.40

Table 7. Percent of isotopic enrichment of Lake Spike Hg solutions as measured by Hintelmann lab.

	^{196}Hg	^{198}Hg	^{199}Hg	^{200}Hg	^{201}Hg	^{202}Hg	^{204}Hg
2001	0.05	0.84	1.67	4.68	1.80	***90.02***	0.94
2002	0.05	0.94	1.68	4.63	1.81	***89.95***	0.95
2003	0.06	1.35	2.08	4.88	1.58	***89.13***	0.92

UPLAND AND WETLAND APPLICATIONS

Several approaches of applying Hg isotopes were considered. One was to spray the isotope using an irrigation system as used for the L. 239 wetland acid addition experiment by Bayley et al. (1986) and Beaty (1987). However, it was concluded that the terrestrial treatment area required for the METAALICUS experiment (43.7 ha) was too large and rugged for this approach, and that aerial application was the only possible means of terrestrial application.

Two approaches to aerial application were considered. First was the use of dry pellets that were coated with Hg isotope. This approach was discarded

because: 1) little of the isotope would have remained on the forest canopy, as occurs during natural deposition and 2) initial tests showed that the Hg isotope would not be leached from the pellets on the forest floor. A second approach was chosen, which was to dissolve the isotopes in lake water and to spray them onto the surface of the forest canopy in a manner that would simulate natural deposition as closely as possible.

Both helicopter and fixed-wing aircraft were considered for the application. Fixed-wing was chosen, primarily because of concern of overspray caused by the helicopter rotor, and the lower cost.

Aerial applications:

Aerial spray criteria: Prior to the beginning of the whole ecosystem manipulation, several pilot studies were done to determine the most appropriate method of application of the Hg isotopes to terrestrial systems. In the first experiment, Hg isotope was applied in a light spray using garden sprayers to a small forested plot (680 m^2) at the ELA (Hintelmann et al. 2002). Hg applied in this manner was considered to be similar to Hg deposited during a light rain event, which is the most common type of rain event at the ELA (~ 50% of the days where precipitation occurred, rainfall was less than 1 mm, K. Beaty, pers. comm.). Only a small portion of the added isotopic Hg was mobile (0.3% was exported via runoff over the season), even during a heavy rain that occurred the day after the application. In contrast, in another pilot experiment where a large amount of water was used to apply the isotope, simulating a 15 mm rain event, 13% of the applied Hg was exported in runoff (D. Krabbenhoft and B. Branfireun, pers. comm.). These studies suggest that applied Hg is more mobile when it is applied in a larger volume. A third set of pilot studies, involving a light spray application to tree foliage, showed that ~60% of wet mercury sprayed onto foliage was lost in two weeks, likely due to the photoreduction of Hg(II) to Hg(0), which then fluxed to the atmosphere (V. St. Louis, pers. comm.). Therefore to minimize this re-emission and to make the experimental applications as natural as possible, the following spray criteria were imposed and used during 2001 and 2002: 1) vegetation should be wet prior to spraying, 2) it should be raining, 3) immediately following application, there should be enough rainfall to facilitate washing the applied mercury off the forest canopy as it would in a natural rain event, and 4) the wind speed should be less than 15 km/hr (4.2 m/s) to minimize drift outside of the sprayblock (the sprayblock is the target area of the watershed to be sprayed) or into the lake.

Conditions where these criteria occured were very rare, and so restricted the number of opportunities to spray. As a result, the terrestrial area was only partially sprayed in 2001 and 2002.

In 2003, the third year of isotope application, it was decided to make the criteria less restrictive to ensure that all the isotopes were applied. The 2003 spray criteria were as follows: 1) enough rainfall to create throughfall should occur within one hour of spraying onto dry foliage and 2) winds should be less than 15 km/hr. Also, if these conditions were not met at the end of the time that the pilot could be on site, the isotope would be sprayed in the early morning or

evening when the light levels were low and winds were light, even if rain was not imminent. Fortunately this eventuality did not occur.

In 2003 amounts of Hg applied to each area were adjusted so that all areas would receive similar cumulative amounts of Hg over the 3 years. Areas that did not get sprayed in previous years were successfully sprayed at a higher rate in 2003, resulting in all areas having received a similar amount of isotope over the 3 years.

Personnel required: Two teams coordinated the application of isotopes and initial ecosystem sampling immediately following each spray event - the isotope application team and the sampling team.

The isotope application team consisted of the pilot, a team leader, a communications/weather person, and a ground crew person. The team leader, who was at the Lake 658 uplands, decided when conditions were correct for spraying and transmitted the order to the pilot to spray. The communications person kept the team up to date with current weather information, which assisted the leader in deciding when to spray. The ground person had three responsibilities. First, to be at the Vermilion Bay airport to ensure that the pilot returned safely. Second, to take water samples from the tank and spray boom immediately after each flight. Third, to help reload the plane with water, and to transfer the next isotope solution into the separatory funnel located in the plane (see detailed methods below).

A typical spray event occurred as follows. When it appeared likely that weather conditions would permit spraying, the team leader would notify the pilot and other team members of the possibility of spraying. The team leader then left the ELA camp for the Lake 658 site. If weather conditions continued to be favourable at Lake 658, the team leader would notify the pilot to take off. Flying time from Vermilion Bay to the Lake 658 basin was about 15 minutes. As soon as the pilot was airborne, the ground crew person left the ELA camp for the Vermilion Bay airport. When the aircraft arrived at the Lake 658 basin the team leader was responsible for deciding when the spray criteria were met. This was done by observing prevailing local conditions and by receiving updated weather forecasts radioed by the communications person. If the criteria had been met, the go-ahead would be given to the pilot who injected the isotopically enriched mercury into the spray tank and began to spray until the whole area was sprayed.

The sampling team consisted of people responsible for the determination of the extent of overspray into the lake, flux of Hg from vegetation, soil, lake surface, sampling of precipitation during and after spraying, and vegetation and soil samples throughout the uplands and wetland. Only overspray data will be presented in this report.

Details of Methods: For the terrestrial isotope application, the Lake 658 watershed was split into seven areas (A,B,C,D,E,F, and P, Figure 5). The large blocks (upland A, B, and C and wetland E) were sprayed by aircraft. The shoreline of the lake (~20 m adjacent to the lake), was not sprayed from the aircraft as these areas are part of the buffer zones of the sprayblocks. These

areas (F -- front of wetland, and D -- shoreline area of uplands, Figure 5) were sprayed by hand since pilot METAALICUS experiments had demonstrated that these could be important sources of terrestrial mercury to the lake (D. Krabbenhoft unpub. data). These shoreline applications are described later. The peninsula (P) was not sprayed because it was considered to be too small and close to the lake to spray by aircraft without risking drift of upland isotope into the lake, but too large and densely forested to be sprayed by hand. Such drift would have confounded the ability to distinguish the input of terrestrial isotope to the lake through normal hydrologic routes such as streamflow and direct runoff.

The upland area to be sprayed by aircraft was initially split into three blocks (A, B, and C in 2001) because the aircraft could not carry enough water to spray the entire upland using a single load. With more experience, we found that the uplands could be sprayed in two loads, and so in 2002 and 2003, blocks A and B were combined, which was sprayed in a single load. This approach had the advantage of reducing the number of spray opportunities that were required to complete the job.

To minimize drift outside of the sprayblocks, the spray boom nozzles, which were controlled by GPS, were programmed to switch on 20 metres after entering a spray block and to switch off 20 metres before exiting a spray block. This resulted in 20-metre buffer zones around the outer edges of each of the sprayblocks. However, application rates (see below) are calculated as if the entire block was evenly sprayed.

Water used to spray from the plane was taken from Eagle Lake at the government dock in Vermilion Bay and transported to the Vermilion Bay Airport in 2000 L and 500 L polypropylene tanks. Chemistry of the water taken from Eagle Lake is given in Table 8. Water samples were analyzed at the ELA Lab and at the FWI Lab. Methods can be found on the internet (Stainton, 2005).

Table 8. Selected water chemistry data for Eagle Lake samples taken June 18, 2001 at the government dock Vermilion Bay, Ontario. Analyses were done by the ELA and Freshwater Institute chemistry laboratories according to Stainton (2005).

Dissolved Organic Carbon	Suspended Particulate Carbon	Chl *a*	Cl	SO_4^{2-}	Conductivity	Alkalinity	In situ pH
µmol/L	µg/L	µg/L	mg/L	mg/L	µS/cm	µeq/L	
410	470	3.01	2.43	2.18	51	319	7.3

This water was acidified (to ~pH 3 by addition of concentrated nitric acid) and covered with a tarp to prevent irradiation of the water by UV light, which could photoactivate the Dissolved Organic Carbon (DOC) and lead to Hg(II) reduction when the isotope solutions were added. The water in the tanks was changed weekly, if it was not used. Acidification of the water also minimized loss of isotope to the tank surfaces of the aircraft.

The aircraft used for the isotope applications was a Cessna 188 AG truck, which is commonly used for pesticide applications in agriculture and forestry. The aircraft contained a 500 L fibreglass tank. Water was mixed in the tank by a hydraulically driven pump, which had an aluminium housing. 250 to 500 L of water was loaded into the plane just before each spraying possibility. Isotope solutions were loaded into a Teflon separatory funnel fixed inside the fibreglass tank (Figure 6). After being given the go-ahead, the pilot pumped the isotope from the separatory funnel into the spray tank using 50 to 100 strokes of a hand operated pressure pump (Figure 6). The isotope was mixed in the fibreglass tank of the plane for about five minutes prior to spraying.

The injection into the tank and mixing was not done until the pilot was at the Lake 658 watershed, and given the go-ahead by radio communication from the team leader. The reason for this was that the plane would be too heavy to land safely on return to Vermilion Bay with a full load of water if the isotope could not be sprayed. Therefore when a spray attempt had to be aborted because of poor weather conditions, the pilot could dump the water but retain the isotope solution in the separatory funnel for the next spray opportunity.

Monitoring of overspray: When Hg isotopes were being sprayed by plane onto the upland and wetland areas surrounding Lake 658, there was always some chance that air currents would cause a portion of the Hg to drift onto the lake surface or outside the basin. Only spray drift onto the lake was quantified. This was done by using two different approaches.

In the first approach, epilimnetic water samples were taken to see how much terrestrial isotope (^{200}Hg and ^{198}Hg) had appeared in the lake water after an aerial spray event. Sampling was not done until at least 24 hours had passed, to allow adequate mixing in the epilimnion. The concentration of terrestrial isotope measured was then multiplied by the epilimnetic volume to provide a quantitative estimate of drift.

In the second approach, in 2002 and 2003, floating collectors were placed on the lake surface prior to aerial spraying, to determine drift of ^{200}Hg and ^{198}Hg onto the lake surface. Collectors were plastic tubs with a surface area of 2,475 cm^2. Collectors were lined with clean plastic bags, and filled with 1.5 L of water acidified with 7.5 ml of concentrated hydrochloric acid (HCl). There were two blank collectors, which were kept covered, and 15 open collectors. All contained acidified water to minimize Hg(II) reduction during the time between spray events and when containers were retrieved (less than 24 hours).

Sample Collection and Analysis: Upon returning to the airport after a spraying event, samples from spray nozzles and the aircraft tank were taken in 250 ml fluorinated polyethylene (FPE) bottles. Samples for overspray (floating collectors and epilimnetic water samples) were collected in either polyethylene terephthalate copolyester (PETG) bottles (floating collectors) or glass or teflon bottles (epilimnetic samples). All samples were preserved with concentrated HCl. Samples were treated with $BrCl_2$ and total mercury was determined by continuous flow cold vapour ICP/MS (Finnigan Element 2) using stannous

chloride as the reducing reagent. A programmed spreadsheet that accounts for procedural blanks and isotopic enrichment of the mercury in the isotope solutions was used to calculate the individual Hg isotope contributions. ^{199}Hg is used as a measure of ambient Hg in the sample. The Limit of Detection (LOD) for total mercury (HgT) is 0.05 ng/L, and for isotopes is 0.5% of the ambient mercury in the sample (methods from Hintelmann, pers. comm.) Samples were analyzed in the laboratories of Dr. R. J. Flett (Flett Research Ltd., Winnipeg, Manitoba), Dr. Cynthia Gilmour (Smithsonian Environmental Research Center), Dr. Holger Hintelmann (Trent University) and Dr. David Krabbenhoft (USGS, Madison, Wisconsin).

Loss of Hg to the aircraft tank: After each spray event, samples of remaining spray solution were taken from the aircraft tank and from the spray nozzles of the aircraft as soon as it returned to Vermilion Bay. This was done to determine if there was any loss of the spike Hg solutions to the aircraft tank and delivery system as it was mixed and passed from the tank to the spray nozzles. Concentrations in these samples were compared to the concentrations expected from the amount of spike Hg added to the tank and the volume of water added to the tank.

In addition, a separate time course experiment was conducted with ambient Hg. The advantage of this experiment was that multiple samples could be taken during the spray period, rather than just at the end. 100 L of Eagle Lake water was acidified to pH 4 and put into the aircraft tank and $HgCl_2$ was added to an initial concentration of 3 mg Hg/L. The contents of the tank were mixed for about one minute prior to the first sampling. The pump that circulates water in the plane to mix and pump during spraying was run continuously for the duration of the experiment, and the aircraft was airborne between sample collection. Duplicate tank samples were taken at predetermined times.

Shoreline spraying: The area of the upland and wetland next to the shoreline was not sprayed from the aircraft to avoid drift of terrestrial Hg isotopes into the lake. Thus in 2002 and 2003 these areas were sprayed by hand, ^{200}Hg to the upland shoreline (Area D) and ^{198}Hg to the wetland shoreline (Area F).

Methods: In 2002, a series of 20 m x 20 m plots were marked around the lake shore (Area D). Winnange Lake water was brought to the spray plots by a barge carrying a large polyethylene water tank. The plots were sprayed with this water using a gas powered water pump and fire hose. The person manually spraying the plots wore a backpack containing a 1 L bottle of isotope solution. This bottle was connected with a hose to an eductor which was controlled by the person spraying. As water passes the eductor, immediately before the nozzle, isotope solution is drawn into the flow of water through the eductor by the venturi effect, the drop in pressure across the eductor. (Figure 7). The application hose was pulled to the back of the plot (furthest from the lake), which was sprayed first, then moved towards the front of the plot (close to shoreline).

The size of the eductor orifice could be changed, by the person spraying, to adjust the rate of addition of the Hg solution, so that the desired time of

application and volume of water could be applied to the plot. Each plot was sprayed until all the Hg solution had been delivered (bottle and connecting line was empty).

The area of the shoreline closest to the lake (~5 m) was not sprayed to avoid direct runoff into the lake. Trees were sprayed as much as possible depending on the height of the trees. Smaller trees got sprayed from top to bottom, whereas larger trees did not get sprayed at the top. Overspray into the lake was monitored on about 10% of the plots. Overspray collectors (plastic tubs) with non-acidified de-ionized water were tied to the barge 1-2 m from the shore during spraying. Contents of collectors were then sampled, and total volume of water in the collectors was recorded. At the time of writing these overspray results are not yet available. There was no visible runoff from spraying that ran directly into the lake. Vegetation samples from trees that were known to have been sprayed were taken 24-36 hours after spraying.

All accessible areas of the wetland shoreline were sprayed, with the exception of areas where streams flowed through the wetland shoreline. One wetland shoreline plot measured 11m x 11m, on the north end of the wetland shoreline, and two additional plots measured 20 m x 20 m.

LAKE APPLICATIONS

General approach

The purpose of the lake addition was to simulate direct rainfall onto the lake surface. A third isotope (^{202}Hg) was used to distinguish this mercury from mercury entering the lake via runoff from the upland or wetland areas.

Application of Lake Spike Hg to the lake surface was done by diluting the Hg into lake water in 20 L carboys, and then adding it slowly into the propeller wash of an electric outboard motor. This is similar to previous whole lake acidification experiments at the ELA (Schindler et al. 1980).

Methods testing

An issue that arose in the planning of the lake additions was how to realistically simulate wet deposition over the open water season in regards to the number, frequency and size of each addition. A second issue was with what to mix the concentrated isotope solution before adding to the lake. It was not possible to reliably collect rainwater before each addition, therefore some other carrier had to be used. Third, previous pilot experiments using limnocorrals in Lake 239 showed that volitilization of Hg could be high after addition of inorganic Hg (Paterson, unpub. data). Perhaps this volitilization could be avoided by many additions with smaller amounts of Hg being added.

The first two issues were addressed by carrying out pilot experiments using a *mer-lux* bioreporter (Golding et al. 2002). These showed that there was seldom any bioavailable Hg(II) in the surface water of the lake (detection limit 0.05 ng bioavaialbe Hg(II)/L), and that the portion of Hg that was bioavailable of Hg (II) to bacteria increased as more Hg was added to lake surface water (C.

Kelly, J. Rudd and M. Holoka, unpub. data). For example, measurement of the % bioavailability of Hg added to Lake 658 surface water showed that an addition of 2 ng Hg/L had a proportionally greater effect on bioavailability than an addition of 1 ng Hg/L. Additions of only 0.5 ng/L had only a slight effect on measurable bioavailable Hg(II). Thus, to avoid increasing bioavailability of Hg(II) over normal levels in the lake's surface water, it was decided that multiple small additions would be made at two week intervals, with each addition increasing the surface water Hg concentration by 0.5 to 1 ng/L. The total Hg load planned for the lake was divided into nine equal additions to simulate wet deposition events onto the lake surface, which is within the range of the number of rain events that would occur normally between June and October in the ELA region.

Another test was done to determine with what to dilute the concentrated Hg solution for the lake application . Hg was first mixed with either distilled water, acidified distilled water, rain, or synthetic rain (oxalate at pH 4) then mixed with Lake 658 water. Bioavailability was then measured. The percentage of bioavailable Hg in these samples was similar, indicating that it did not matter (with respect to bioavailability) what the Hg was mixed in first, prior to addition to the lake.

The third issue of high volatilization after addition was also tested. The goal of the test was to estimate potential volitilization of Hg injected at one metre depth at dusk. Six 1-L teflon bottles were filled completely with L. 658 water and incubated at one metre in Lake 240, beginning at dusk. The bottles were retrieved five hours later and dissolved gaseous mercury (DGM) was measured as an estimate of the amount of Hg that would volatilize. Two bottles did not get any added Hg, two received 1.3 ng of $HgCl_2$ prepared in Lake 658 water, and two received 1.3 ng of $HgCl_2$ prepared in de-ionized water. Only 3 to 5% of the spike was reduced (and measured as DGM) under these conditions. There was no significant difference incubations with lake water or de-ionized water (M. Amyot, pers. comm.).

In order to dilute the Lake Spike Hg before adding to the lake, 20 mL of the concentrated Hg (approximately 2.6 g/L) was mixed with lake water in 20 L carboys. The carboy material (fluoridated polyethylene, or FPE) was tested for possible Hg adsorption and for methylation. This was done using smaller FPE bottles (250 mL), Lake 658 water acidified with HNO_3 to pH 3, and Hg added to a final concentration of 3.5 ng/L. HgT and MeHg were measured by Flett Research on samples provided. There was no loss of Hg from the solution, and no MeHg formed during the two hour experiment.

Lake Spike Application Methods

24 hours prior to the lake isotope applications, two - 20L carboys (FLPE) were filled with Lake 658 water and put in the dark in an attempt to minimize the presence of photo-activated reductants that could lead to reduction of Hg(II) in the solution. Isotope was added to the carboys and allowed to equilibrate and mix for one hour before application began.

Application began at sunset, again to avoid photoreduction while the isotope solution was being mixed into the surface water of the lake. The isotope solution was injected at 70 cm depth into the propeller wash of the trolling motors by use of a peristaltic pump. The lake area was split roughly in half with one boat applying isotope to each half to ensure even distribution of Lake Spike Hg. The applications took about 1.5 hours to complete while criss-crossing the lake. Previous work at ELA demonstrated that chemicals added to lakes mix quickly into the epilimnion throughout the lake, e.g., when ^{14}C was added to L. 226 in the evening, samples from the following morning showed even mixing throughout the epilimnion (Bower et al. 1987). Isotope was not applied near the outflow to avoid immediate loss out the outflow, and was not applied close to the wetland where it is shallow to avoid disruption of sediments.

Monitoring of lake applications

Before each application, water samples were taken at the centre buoy of each basin and filtered in the field either as part of a profile or surface water samples. This resulted in two types of samples; filtered water, and particulates (captured on Whatman Quartz QMA filters). Two surface water samples were also taken in each basin (unfiltered) after each application to check for even mixing. Water samples were analyzed for HgT as described above. QMA filters were analyzed for HgT by the same method as water samples with a digestion in a mixture of concentrated sulphuric and nitric acids instead of the $BrCl_2$ treatment. The limit of detection (LOD) for HgT on particulates is 0.12ng/L (methods from Hintelmann lab).

RESULTS AND DISCUSSION

UPLAND AND WETLAND AERIAL APPLICATIONS

Aerial spray events

Dates and times of the upland and wetland isotope applications are given in Table 9.

Table 9. Dates and times of upland and wetland aerial applications.

Date	Spray block	Time Began	Time Ended
13-June-01	A	10:44	11:10
18-June-01	B	17:03	17:23
27-June-01	E	19:26	19:38
28-May-02	A	12:03	12:19
28-May-02	B	12:21	12:38
28-May-02	C	13:31	13:55
18-May-03	C	09:56	10:12
18-May-03	A+B	11:10	12:08
18-May-03	E	06:32	06:59

Weather conditions

The most important spray criteria were timing of rainfall and wind velocity, and these determined the relative success of a particular spray event. Selected meteorological data associated with spray events are presented in Table 10, and rainfall is shown in Figures 8-10.

Table 10. Wind conditions, temperature and relative humidity for each spray event.

Spray Event	Average Temp (°C)	Avg. Relative Humidity (%)	Average Wind speed (m/s)	Avg. Gust speed (m/s)	Max. Gust speed (m/s)	Avg. Wind Direction (Degrees)
Area A, 13-June-01*	14.5	82	2.7	no data	5.83	no data
Area B, 18-June-01*	19	66	3.4	no data	8	no data
Area E, 27-June-01*	18	92	1.1	no data	3.3	no data
Area A, 28-May-02**	13.5	82.5	0.5	no data	2.5	no data
Area B, 28-May-02**	13	92	0	no data	1.5	no data
Area C, 28-May-02**	12.5	93.5	0.5	no data	2.5	no data
Area A+B, 18-May-03***	13.95	89.34	2.32	2.74	5.57	156.68
Area C 18-May-03***	11.62	96.19	1.34	1.56	2.78	151.59
Area E 18-May-03***	11.63	96.56	1.01	1.16	2.41	155.48

* data are from meteorological tower on south side, 15 min. averages, ** data from Lake 658 met raft station, data are 15 min. averages, *** data from north side meteorological station (located at the highest point of the upland) data are averages of one minute averages of 10 second interval measurements.

In 2001 area A was sprayed after the canopy was wet. However it was not raining during application and did not rain for one and a half hours after spraying ended (total rain volume was 7.7 mm, mostly after the spray, Figure 8). The canopy was not wet before area B was sprayed, however it did rain a significant amount (34.3 mm total) starting about one hour after spraying. The spraying of the wetland (area E) in 2001 met all the criteria with a large rainfall immediately after spraying (total 53.6 mm, Figure 8).

In 2002 the canopy was wet before all 3 spray events, however rain continued only after spraying areas A&B, and stopped before spraying area C (total 4.72 mm, Figure 9).

For the first two spray events of 2003 (the wetland E and upland C) conditions were very good and would have met the 2001-2002 criteria. The last spray event of 2003 (Upland A/B) occurred under conditions that were close to all others. In this case the foliage was wet prior to spraying, but further rainfall did not occur until about four hours after application (Figure 10). Table 11 summarizes conditions associated with each spray event. Observations of canopy wetness prior to spray, rainfall during application, and wind conditions were made by the team leader before and during spraying.

Table 11. Aerial spray criteria, and whether each one was met for each individual spray event (* indicates that criterion was fulfilled adequately), and canopy development.

Spray event	Canopy Wet Prior to spray	Rainfall During Application	Wind light and away from lake	Hg washed off canopy after spray	Deciduous canopy development
Upland A 2001	*		*		full
Upland B 2001			*	*	full
Wetland 2001	*	*	*	*	full
Upland A/B 2002	*	*	*		low
Upland C 2002	*		*		low
Upland A/B 2003	*		*	*	full
Upland C 2003	*	*		*	full
Wetland 2003	*	*	*	*	full

Aerial spray tracks

Aerial spray tracks for 2001, 2002, and 2003 are shown in Figures 11-13. These data are the GPS position of the aircraft when the spray booms were on. However, after leaving the aircraft, spray droplets did not fall straight down, and so these tracks are not a true representation of exactly where the isotope fell when it reached the watershed. Spray tracks were intended to be 20 m apart. This spacing was chosen because under ideal conditions, at the height the aircraft flies (about 40' above the treetops) the spray would spread to cover the distance between each track evenly. In practice, the spacing was not equidistant and at times there was overlap. This happened for two reasons: 1) weather conditions and terrain prevented the pilot from flying in an exact straight line, 2) the pilot and team leader had the option of modifying the application pattern in response to local conditions. For example, in the 2002 spraying of the south side of the basin (block C) the pilot decided to leave a larger buffer zone around the lake because the wind was coming from the south. This was done to avoid drift

into Lake 658. Also, for the 2003 block A/B spraying, the team leader asked the pilot to spray some of the isotope about half way down the sprayblock, instead of spraying the northern part of the sprayblock. This was done because of the south wind that would have otherwise caused the isotope to drift out of the sprayblock. Also in 2001 part of the Upland Spike Hg was sprayed outside the watershed boundary (NE corner, Figure 11), this was because of inaccurate maps at that time.

Because of the small size and location of the wetland (block E), the activation of the spray boom nozzles was done manually rather than by computer. Several of these tracks overlapped because of the narrowness of the wetland. Also, in 2003, some of the spray tracks went over a small portion of the upland. The wind was coming from the south at the time, and so the spray fell somewhat to the north of the actual spray tracks. Also there were some times when spraying started too early or stopped too late at the lake end of the wetland.

Hg loads, spray volumes, areas

The amount of Hg added to the plane tank for each spray event is shown in Table 12. Also shown are the total areas of each spray block, and the volume of acidified lake water added to the plane tank to dilute the isotope solutions before spraying. As shown later, the amount of Hg added to the plane tank was not all delivered from the plane during spraying.

Table 12. Areas, amount of Hg put in plane, and spray volumes for each aerial spray application to Lake 658 uplands and wetland

Date	Spray block	Area (ha)	Hg (g) added to plane tank	Isotope	Spray volume (L)
13-June-01	A	10.52	3.41	^{200}Hg	500
18-June-01	B	11.05	3.39	^{200}Hg	500
27-June-01	E	1.51	0.45	^{198}Hg	250
28-May-02	A+B	21.57	2.65	^{200}Hg	360
28-May-02	C	15.93	8.19	^{200}Hg	240
18-May-03	A+B	21.57	6.62	^{200}Hg	400
18-May-03	C	15.93	3.62	^{200}Hg	250
18-May-03	E	1.51	0.905	^{198}Hg	250

Monitoring of Overspray

In 2002, three of the 15 surface collectors had concentrations of Upland Spike Hg that were appreciable (Figure 14, Table 13). Two calculation methods were used to extrapolate from these measurements to estimate the total amount of overspray to the lake surface. The first used the average overspray dose for the 15 collectors (242 ng/m^2 of Upland Spike Hg), and applied this number to the entire lake area. The second made the assumption that the overspray would

decline with distance from the shoreline, and would not be significant beyond a 30 m distance from the shoreline. This resulted in an estimate of 170 ng/m^2 Upland Spike Hg onto the lake surface. On a whole lake basis, estimates of overspray from the terrestrial areas onto the lake from these two approaches were 20 and 14 mg Upland Spike Hg, respectively.

Table 13. Upland Spike Hg measured in overspray collectors, May 28, 2002. Locations of collectors and isotope results shown in Figure 14. Samples analyzed in Gilmour lab.

Collector	Concentration of Upland Spike Hg (ng/m^2)
A (blank)	0
B (blank)	0
C	1,594
D	482
E	32
F	32
G	32
H	3
I	36
J	35
K	12
L	11
M	1,542
N	22
O	5

In 2003, the surface collector results showed a pattern of higher deposition of Upland Spike Hg along the south half of the lake, and low or undetectable deposition along the north half of the lake (Figure 15, Table 14). All collectors showed extremely low or undetectable Wetland Spike Hg, except for F and G, located very near the edge of the wetland. Given the even distribution of collectors over the lake surface (Figure 15), the mean rate of overspray of the 17 collectors, was calculated to be 22 ng/m^2 of Wetland Spike Hg, and 412 ng/m^2 of Upland Spike Hg. The whole lake totals (multiplying by the lake area of 83,900 m^2) were 2 mg for Wetland Spike Hg and 35 mg for Upland Spike Hg.

As mentioned above, an estimate of overspray, or drift, of terrestrial isotope applications was also made from measurements of concentrations of terrestrial isotopes in epilimnetic water, following a spray event and after enough time had passed to ensure epilimnetic mixing. The epilimnetic concentrations, and calculations of total upland and wetland overspray amounts are shown for 2001 and 2002 (Table 15) and for 2003 (Table 16). In 2003, estimates were done using a range of possible epilimnetic depths on each depth, because the intervals chosen for temperature profiles were not fine enough to distinguish the exact bottom of the epilimnion.

Table 14. Upland Spike Hg and Wetland Spike Hg measured in overspray collectors May 18, 2003. Locations of collectors and isotope results are shown in Figure 15. Samples analyzed in USGS lab.

Collector	Wetland Spike Hg ng/m^2	Upland Spike Hg ng/m^2
A (blank)	0	2
B (blank)	1	5
C	2	567
D	7	790
E	3	423
F	218	2,013
G	104	2,229
H	2	42
I	18	263
J	0	21
K	2	48
L	1	54
M	5	206
N	2	144
O	0	4
P	1	11
R	13	181

Table 15. Estimates of amount of Upland Spike Hg in Lake 658 epilimnetic waters following aerial Hg applications on June 18, 2001 and May 28, 2002. Samples analyzed in Hintelmann lab.

Date	Site*	Epilim-nion Depth (m)	Epilimnion Vol (m^3 x10^3)	Wetland Spike Hg (ng/L)	Upland Spike Hg (ng/L)	Estimated Overspray of Upland Spike Hg to lake (mg)
20-Jun-01	West	3	213	not detected	0.1	21
21-Jun-01	E/W 2 m	3	213	not detected	0.05	11
3-Jun-02	E/W 2 m	2	148	not detected	0.12	18
5-Jun-02	West	2	148	not detected	0.11	16

*"West" means that the sample was taken from the west basin only "E/W 2 m" is an integrated sample from both basins at 2 m depth.

Table 16. Estimates of amount of Upland and Wetland Spike Hg in Lake 658 epilimnetic water following aerial Hg applications on May 18, 2003. Samples analyzed in Hintelmann lab.

Date	Epilimnion Depth (m)	Estimated overspray of Wetland Spike Hg to lake (mg)	Estimated overspray of Upland Spike Hg to lake (mg)
19-May-03	2 to 3	6 to 10	27 to 47
20-May-03	2 to 3	13 to 18	47 to 67
21-May-03	2 to 3	9 to 13	35 to 50

* ranges were calculated because exact depths of epilimnion were not available, and often these depths were different in the east and west basins.

For the two years when both methods of estimating overspray (surface collectors and epilimnetic sampling) were used, the results were similar (Table 17). In 2002, the surface collector measurements gave an estimate of 14-20 mg of Upland Spike Hg while the epilimnetic surface sampling gave an estimate of 16-18 mg of Upland Spike. In 2003, the surface collectors gave an estimate of 35 mg of Upland Spike Hg compared to a range of 27 - 68 mg from the epilimnetic samples. The wetland overspray estimate from the surface collectors (2 mg Wetland Spike Hg) was less than from the epilimnetic samples (6 to 18 mg Wetland Spike Hg), but both estimates were very small compared to the total amount of Hg applied to the wetland in 2003 (Table 17).

Table 17. Estimates of % of aerial sprays that drifted onto the lake surface.

Date	Days since spike	Epilimnion or Collectors	Estimated overspray of Upland Spike Hg (mg)	Estimated overspray of Wetland Spike Hg (mg)	% of yearly Upland Spike Hg	% of yearly Wetland Spike Hg
20-Jun-01	2	Epi	21	-	0.69	-
21-Jun-01	3	Epi	11	-	0.34	-
28-May-02	0	Collector	14-20	-	0.21	-
3-Jun-02	5	Epi	18	-	0.18	-
5-Jun-02	7	Epi	16	-	0.17	-
18-May-03	0	Collector	35	2	0.4	0.3
19-May-03	1	Epi	27-47	6-11	0.3-0.6	0.7-1.4
20-May-03	2	Epi	47-68	13-18	0.5-0.8	1.6-2.2
21-May-03	3	Epi	35-50	9-13	0.4-0.6	1.1-1.6

After each aerial application, there could have been some wetland or terrestrial spike movement into the lake through direct runoff after the spike landed on the terrestrial surface. However, monitoring of upland isotope in the north inflow stream (D. Krabbenhoft, pers. comm.) showed that the amount entering in this way was insignificant compared to the amount measured in the lake water after the spray events. Also, the agreement between the method of

using surface collectors and epilimnetic water samples (Table 17) indicated that the isotopes found in the lake water entered from the air.

The amounts that drifted onto the lake surface were compared to the amounts of Hg that exited the plane (see later results and Table 22) on each spray date for which we have data on drift (Table 17). In all cases, the proportion of aerial spikes estimated to have drifted onto the lake surface was extremely low (Table 17). This was a positive outcome, as drift into the lake would mean that less spike Hg was deposited onto the surfaces for which it was intended. In addition to drifting onto the lake surfaces, there could also have been some drift onto terrestrial areas outside the Lake 658 watershed. Since the lake occupies about a third of the perimeter around the area of the spray blocks A/B or C, it is a good indicator of drift, but it would receive some fraction less than the total drift. This fraction would depend primarily on wind speed and direction and on the location of the airplane with respect to the spray block boundaries. As indicated earlier, the pilot used discretion in this regard, to minimize drift. This, and the low masses indicated by the overspray collectors and the lake samples, lead us to conclude that nearly all of the isotope that left the aircraft did fall onto the Lake 658 watershed.

Another concern was that overspray might add significantly to the amount of Hg being applied directly to the lake as Lake Spike Hg and that this would make it difficult to interpret results pertaining to upland and wetland isotopes. Compared to the amounts added each year to the lake, the overspray estimates for Upland Spike Hg were only 0.8 to 4% of annual Lake Spike Hg additions, and the overspray estimates for Wetland Spike Hg were only 0.1 to 1% of annual Lake Spike Hg additions. However, if similarly small proportions of Upland or Wetland Spike Hg are found in methyl Hg or biota, it would be difficult to tell if these came from overspray or from streams and runoff.

Loss of Spike Hg to aircraft

After each spray event, samples were taken from the aircraft tank and from the spray nozzles. A summary of the analyses of these samples is presented in Table 18.

There was no difference in isotope concentrations between samples taken from the fiberglass tank and boom nozzles (Table 18) demonstrating that the stainless steel spray booms were not responsible for any of this loss. There was also no difference in isotopic content between the spikes added, and the spray and nozzle samples (D. Krabbenhoft, pers comm.), demonstrating that there was no contamination of the spikes with natural Hg that might have been associated with the tank and spray apparatus.

Table 18. Raw Data for Analyses of Plane tank samples (Date, sprayblock, time sampled, hours since spray, and Spike Hg concentration).

Date	Spray-block	Sample	Hours since spray	Spike Hg Con. (mg/L)
June 13/01	A	Nozzle*	24	4.73
June 13/01	A	Nozzle*	24	4.05
June 13/01	A	Tank*	24	4.57
June 18/01	B	Nozzle*	1	5.50
June 18/01	B	Tank*	1	4.84
June 18/01	B	Tank*	1	5.11
May 28/02	A+B	Tank	1	5.31
May 28/02	A+B	Nozzle	1	5.41
May 28/02	C	Tank	1	25.00
May 28/02	C	Nozzle	1	26.60
May 18/03	C	Tank	0.83	12.3
May 18/03	C	Nozzle 1	0.83	12.9
May 18/03	C	Nozzle 2	0.83	12.5
May 18/03	A+B	Tank 1	1.25	17.6
May 18/03	A+B	Tank 2	1.25	15.3
May 18/03	A+B	Nozzle	1.25	17.1
May 18/03	E	Tank	0.75	4.82
May 18/03	E	Tank	0.75	4.39
May 18/03	E.	Nozzle	0.75	3.98
May 18/03	E	Tank Rinse	1	0.04
May 18/03	E.	Tank Rinse	1	0.04

*In 2001 samples were analyzed at the USGS lab in Madison WI. All other samples were analyzed by Flett Research Ltd, Winnipeg, MB.

In 2001 and 2002 comparison of the post-spray sample concentrations (the average of all tank and nozzle samples) with the calculated initial concentrations of Hg in the airplane tank indicated that there was likely some loss of mercury isotopes to the aircraft, tank and pumps before the isotopes exited the spray nozzles (Table 19). The 2003 data showed post-spray concentrations near or above the calculated initial concentrations. Spray volumes were not measured as accurately in 2003; thus we have less confidence in these results as useful in estimating differences between the concentrations we expected and actual spray concentrations.

Table 19. Amount of Hg in each isotopic solution, spray water volumes in airplane tank, calculated initial Hg concentration in aircraft tank immediately after isotope injection, and concentrations of nozzle samples after return to the airport.

Date	Spray block	Hg added to tank (g)	Volume (L)	Calculated Initial Concen-tration (mg Hg/L)	Average Post Spray Sample Concentration (mg Hg/L)	Ratio of Post Spray sample To Calculated Initial concentration
June 13/01	A	3.41	500	6.8	4.5*	.66
June 18/01	B	3.39	500	6.8	5.1*	.76
June 27/01	E	0.45	250	1.8	Sample lost	
May 28/02	A/B	2.65	360	7.4	5.36	.71
May 28/02	C	8.19	240	34.1	25.80	.74
May 18/03	A/B	6.62	400	16.6	16.7	1.01
May 18/03	C	3.62	250	14.5	12.6	.87
May 18/03	E	0.905	250	3.6	4.4	1.21

* In 2001 samples were analyzed in USGS. All other samples were analyzed by Flett Research Ltd.

The problems of uncertainty over some of the tank volumes, and inability to sample at the actual time of spraying were overcome with the time-course experiment specifically designed to look at loss of Hg from the airplane tank during spraying. In this experiment, loss of Hg to the tank showed a linear relationship with time (Table 20), described by the following equation, $y = -0.0063x + 0.993$, where y = proportion of Hg remaining in the tank, and x = is the number of minutes the solution was in the aircraft, $r^2 = 0.97$, Figure 16).

The average proportion of Hg leaving the aircraft can be estimated by the equation using the midpoint of the length of time of spraying (plus 5 minutes prior to spraying during which the isotope was mixed into the water in the tank) as the x value (Table 21).

Table 20. Results of May 2003 test of Hg adsorption to aircraft tank and pump under flight conditions with pump mixing the tank contents continuously.

Time (minutes)	Tank Sample ID	Analytical duplicates	Hg mg/L	Average Hg mg/L	Relative to T_0
1	1A		3.15	3.12	1.00
1	1B		3.08		
7	2A		2.84	3.01	0.96
7	2B		3.22		
7	2B	Duplicate	3.12		
26	3A		2.48	2.45	0.78
26	3B		2.41		
58	4A		2	2.01	0.64
58	4A	Duplicate	2.04		
58	4B		1.99		

Table 21. Estimate of proportion of Hg leaving aircraft during Lake 658 watershed spray events.

Date	Spray block	Total Length of Spray + 5 mins mixing time (minutes)	Estimate of Proportion Leaving aircraft
13-Jun-01	A	31	0.90
18-Jun-01	B	25	0.91
27-Jun-01	E	17	0.94
28-May-02	A+B	38	0.87
28-May-02	C	29	0.90
18-May-03	A+B	63	0.79
18-May-03	C	21	0.93
18-May-03	E	32	0.89

Estimates of Aerial application rates

Estimates of aerial application rates for each spray event (Table 22) were calculated based on the amounts of Spike Hg added to the airplane tank, and the proportion of Hg leaving the aircraft as shown in Table 21).

Table 22. Estimated aerial application rates for each spray event (using estimate of proportion of Hg leaving aircraft in Table 21).

Date	Area	Hg leaving aircraft (g)	Wetland Spike Hg ($\mu g/m^2$)	Upland Spike Hg ($\mu g/m^2$)
13-June-01	A	3.05	-	29.02
18-June-01	B	3.10	-	28.05
27-June-01	E	0.42	28.06	-
28-May-02	A/B	2.31	-	10.73
28-May-02	C	7.38	-	46.35
18-May-03	A/B	5.26	-	24.39
18-May-03	C	3.36	-	21.06
18-May-03	E	0.81	53.60	-

Table 23. Estimated aerial application rates, three year totals for 2001, 2002 and 2003.

Area	Hg Leaving aircraft (g)	Wetland Spike Hg ($\mu g/m^2$)	Upland Spike Hg ($\mu g/m^2$)
A/B	13.73	-	64
C	10.74	-	67
E	1.23	82	-
P	0	0	0

* These numbers do not include shoreline spraying, see below.

In the calculation of application rates it is assumed that all of the Hg sprayed in the spray block stayed in that spray block and that it gets deposited evenly. However there was a small amount of drift during spraying, some of which is onto the lake (estimated in this report) and likely some drift outside of the watershed area. Also, in two cases (NE corner in 2001, and SW of wetland in 2002) some of the spray tracks are outside the watershed boundary. This is partly due to the use of inaccurate maps at that time. The distribution of Hg deposition is likely not homogeneous since the spray tracks are not evenly distributed across the spray blocks. Therefore some areas may have more than the calculated application rate and other places less.

SHORELINE APPLICATIONS

Upland shoreline applications

Due to difficulties with the spraying apparatus, only six upland plots were sprayed in 2002 (Plot #'s 112-113, 113-114, 115-116, 1-2, 3-4 and 4-5, as shown in Figure 17). These six upland shoreline plots were sprayed on September 17-19, 2002.

In 2003, the goal was to apply a total of three years' dose to all the upland shoreline plots. Therefore, each of the six plots sprayed in 2002 received an additional dose of only 6.42 mg Upland Spike Hg (16 $\mu g/m^2$) in 2003. The remaining plots (that were not sprayed in 2002) received a three year dose of

30.1 mg Upland Spike Hg (75.2 µg/m^2). The spraying was done on June 9 to 12, 2003. The isotope purity of Upland Spike Hg applied in 2003 was 80.45% ^{200}Hg and was a mixture of 2002 and the 2003 blend. The locations of all the shoreline plots sprayed in 2003 are shown in Figure 18, and the total amounts sprayed over the two-year period are summarized in Table 24 and Figure 18.

It should be noted that these plots only covered about half of the entire shoreline. The remainder of the shoreline was not sprayed because of inaccessibility.

Table 24. Summary of Hg applications to upland shorelines.

Year	Upland Edge Plot #'s	Individual Plot Area (m^2)	Upland Spike Hg per Plot (g)	Upland Spike Hg (µg /m^2)
2002	112-113,113-114, 115-116, 1-2, 3-4, 4-5	400	0.0236	59.1
2003	112-113, 113-114, 115-116, 1-2, 3-4, 5-6	400	0.0064	16.0
2003	43 other upland plots (see Figure 18)	400	0.0300	75.2
Two year totals	All upland shoreline plots			75.2

Wetland shoreline applications

The wetland edge was not sprayed in 2001. The amounts of mercury applied to each plot, in 2002 (September 26 and October 2) and 2003 (June 12) are shown in Table 25. The isotopic purities of the spikes applied to each plot each year are also provided.

Table 25. Summary of Hg applications to wetland shorelines.

Year	Wetland Edge Plot #	Area (m^2)	^{198}Hg % purity and bottle	Wetland Spike Hg per plot (g)	**Wetland Spike Hg (µg /m^2)**
2002	1 (north)	121	90.5 % (2001 bottle E)	0.0069	**57.2**
2002	2	400	90.5 % (2002 bottle F)	0.0192	**48.0**
2002	3	400	90.5 % (2002 bottle F	0.0192	**48.0**
2003	1+2 combined	521	90.84 % (2003 bottle F)	0.0145	**27.9**
2003	3	400	90.84 % (2003 bottle F)	0.0110	**27.4**
Two year totals	1	121		0.0103	**85.1**
	2	400		0.0304	**75.9**
	3	**400**		**0.0302**	**75.4**

LAKE ADDITIONS

Details of spikes

Dates of Lake Hg applications: Isotopically enriched Hg was added to Lake 658 over 18 weeks (at two week intervals) in the summers of 2001 to 2003. Some of the additions were delayed a day because of thunderstorms. With each Hg addition to the lake the epilimnion depths were determined (to the nearest 25 cm) from temperature profiles obtained during water chemistry sampling (usually the day before the application, see Tables 26-28).

Table 26. Amount of Lake Spike Hg added and epilimnion (Epi) depths and volumes in 2001. Volumes are interpolated from data in Figure 3.

Date	Lake Spike Hg added (mg)	Epi Depth West (m)	Epi Depth East (m)	Average Epi depth (m)	Epi Volume ($x10^3$ m^3)
19-Jun-01	206.13	3.0	3.0	3.0	213
03-Jul-01	206.33	2.0	2.75	2.38	172
17-Jul-01	205.25	1.5	1.5	1.5	112
01-Aug-01	204.95	2.25	2.0	2.13	156
15-Aug-01	204.7	3.0	3.0	3.0	213
28-Aug-01	206.28	2.5	2.5	2.5	180
11-Sep-01	206.13	3.5	3.75	3.63	250
25-Sep-01	206.35	4.25	4.5	4.38	294
09-Oct-01	206.3	5.5	5.75	5.63	360
TOTAL	1852.4				

Table 27. Amount of Lake Spike Hg added and epilimnion (Epi) depths and volumes in 2002. Volumes are interpolated from data in Figure 3.

Date	Lake Spike Hg added (mg)	Epi Depth West (m)	Epi Depth East (m)	Average Epi depth (m)	Epi Volume ($x10^3$ m^3)
04-Jun-02	208.47	2.0	2.0	2.0	148
18-Jun-02	207.9	1.25	1.5	1.38	104
02-Jul-02	207.3	2.0	2.0	2.0	148
16-Jul-02	206.67	1.25	0.5	0.88	68
30-Jul-02	206.92	2.25	2.0	2.13	156
13-Aug-02	206.8	2.0	2.75	2.38	172
27-Aug-02	206.37	2.0	2.0	2.0	148
10-Sep-02	206.55	1.25	1.0	1.13	86
24-Sep-02	199.08	4.0	4.0	4.0	272
TOTAL	1856.05				

Table 28. Amount of Lake Spike Hg added and epilimnion (Epi) depths and volumes in 2003. Volumes are interpolated from data in Figure 3.

Date	Lake Spike Hg added (mg)	Epi Depth West (m)	Epi Depth East (m)	Average Epi depth (m)	Epi Volume ($x10^3$ m^3)
10-Jun-03	208.18	2.0	2.5	2.25	164
24-Jun-03	207.83	2.0	2.0	2.0	148
09-Jul-03	207.75	2.75	3.0	2.88	205
22-Jul-03	207.53	3.0	2.5	2.75	196
06-Aug-03	208.38	3.0	3.0	3.0	213
20-Aug-03	208.23	3.0	3.0	3.0	213
03-Sep-03	208.28	4.0	4.0	4.0	272
16-Sep-03	208.18	4.25	4.0	4.0	280
30-Sep-03	207.91	6.0	6.0	6.0	378
Total	1872.24				

Measurement of Hg in surface water before each addition, the epilimnion volume on the date of addition, and the amount of Lake Spike Hg added was used to calculate expected Hg concentration after each Lake Spike Hg addition (Tables 29-31). These numbers were not expected to agree exactly, because there would be some volatilization, and the epilimnetic bottom depth was not precisely known. The purpose of this exercise was to see if there was general agreement between the concentration predicted and the concentration measured.

Table 29. Lake 658 surface water Lake Spike Hg concentration before and after each application and comparison of actual vs. expected increase in Hg in 2001.

Date	Pre-addition Lake Spike Hg (ng/L)*	Post-addition Lake Spike Hg (ng/L)*	Expected Lake Spike Hg increase (ng/L)	Actual Lake Spike Hg increase (ng/L)	% of expected
19-Jun-01	0	1.17	0.97	1.17	121%
03-Jul-01	0.49	1.45	1.19	0.96	80%
17-Jul-01	0.78	2.26	1.82	1.48	81%
01-Aug-01	1.19	2.06	1.31	0.87	66%
15-Aug-01	1.25	1.89	0.96	0.64	67%
28-Aug-01	1.64	No data	1.14		
11-Sep-01	1.55	2.34	0.82	0.79	96%
25-Sep-01	1.65	2.52	0.7	0.87	124%
09-Oct-01	1.63	2.62	0.57	0.99	173%

*Surface water samples analyzed in Hintelmann lab, Trent University.

Table 30. Lake 658 surface water Lake Spike Hg concentration before and after each application and comparison of actual vs. expected increase in Hg in 2002.

Date	Pre-addition Lake Spike Hg (ng/L)*	Post-addition Lake Spike Hg (ng/L)*	Expected Lake Spike Hg increase (ng/L)	Actual Lake Spike Hg increase (ng/L)	% of expected
04-Jun-02	0.49	2.02	1.41	1.53	109%
18-Jun-02	0.91	2.36	1.99	1.45	73%
02-Jul-02	1.44	2.17	1.4	0.73	52%
16-Jul-02	1.21	2.47	3.02	1.26	42%
30-Jul-02	1.69	2.57	1.32	0.88	67%
13-Aug-02	1.55	2.81	1.2	1.26	105%
27-Aug-02	1.52	2.35	1.39	0.83	60%
10-Sep-02	2.93	2.68	2.38	-0.25	-11%
24-Sep-02	2.27	2.51	0.73	0.24	33%

*Surface water samples analyzed in Hintelmann lab, Trent University.

Table 31. Lake 658 surface water Lake Spike Hg concentration before and after each application and comparison of actual vs. expected increase in Hg in 2003.

Date	Pre-addition Lake Spike Hg (ng/L)*	Post-addition Lake Spike Hg (ng/L)*	Expected Lake Spike Hg increase (ng/L)	Actual Lake Spike Hg increase (ng/L)	% of expected
10-Jun-03	0.45	1.69	1.27	1.24	98%
24-Jun-03	0.85	1.96	1.4	1.11	79%
09-Jul-03	1.05	1.76	1.01	0.71	70%
22-Jul-03	1.42	2.44	1.05	1.02	97%
06-Aug-03	1.54	2.25	0.98	0.71	73%
20-Aug-03	1.65	2.38	0.98	0.73	75%
03-Sep-03	1.55	2.13	0.76	0.58	76%
16-Sep-03	1.65	2.37	0.74	0.72	97%
30-Sep-03	1.55	1.93	0.55	0.38	69%

*Surface water samples analyzed in Hintelmann lab, Trent University.

3 year total Lake spike Hg additions to the Lake

Table 32. Total amounts of Hg added to Lake 658, and application rates over the three years.

Lake	Lake Spike Hg (mg)	Lake Spike Hg ($\mu g/m^2/yr$)
2001	1,852.40	22.07
2002	1,856.05	22.12
2003	1,872.24	22.31
3 year total	**5,580.69**	**66.50**

SUMMARY

Over the first three years of the METAALICUS project, the loadings to the lake were equal in all years (Table 32), while the loadings to the watershed areas were different in different years (Table 22). These year to year differences will be important to take into account in the interpretation of the responses of the watershed and lake to the Hg loadings. By the end of 3 years, however, the accumulated loadings to the watershed areas were reasonably similar, with the Upland areas receiving somewhat less than the lake, per unit area, and the wetland area receiving somewhat more (Table 33). The cumulative watershed loading rates in Table 33 take into account loss of Hg to the aircraft and Hg added through the shoreline spraying done by hand. Over 3 years, the whole ecosystem (watershed plus lake) received 32.8 g of total Hg, with an average loading rate of approximately 63 ug HgT/m^2.

Table 33. Summary of Hg applications to each ecosystem component including shoreline spraying, 2001-2003.

	Upland	Wetland	Lake	Terrestrial (Upland and Wetland)	Whole Ecosystem
Isotope	^{200}Hg	^{198}Hg	^{202}Hg		
Average Isotope Purity	80.5%	90.6%	90.8%		
Mercury applied (g HgT)	25.94	1.30	5.58	27.24	32.82
Area (ha)	42.09	1.66	8.39	43.75	52.14
3 year Application Rate ($\mu g\ HgT/m^2$)	61.63	78.45	66.50	62.26	62.93

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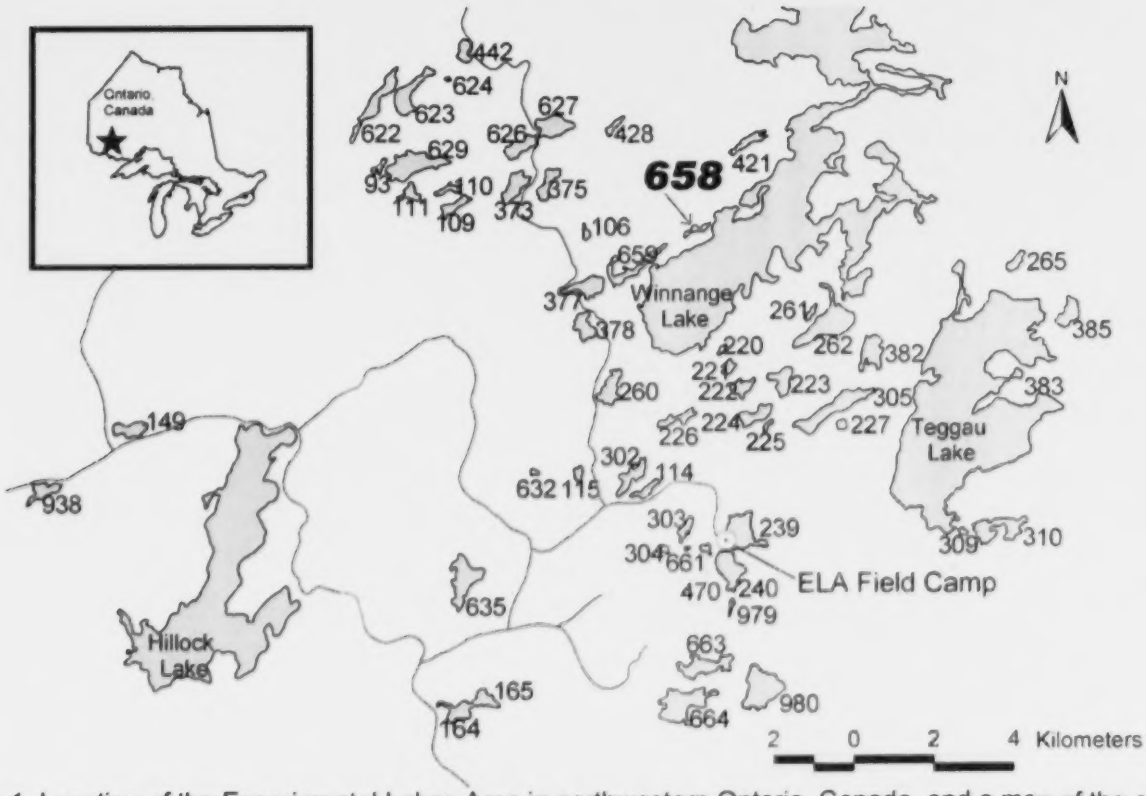

Figure 1. Location of the Experimental Lakes Area in northwestern Ontario, Canada, and a map of the area showing Lake 658. Figure modified from Gunn, J.M., R.J. Steedman, and R.A. Ryder, editors. 2003. Boreal Shield Watersheds: Lake trout ecosystems in a changing environment. Lewis Publishers, CRC press. 501p.

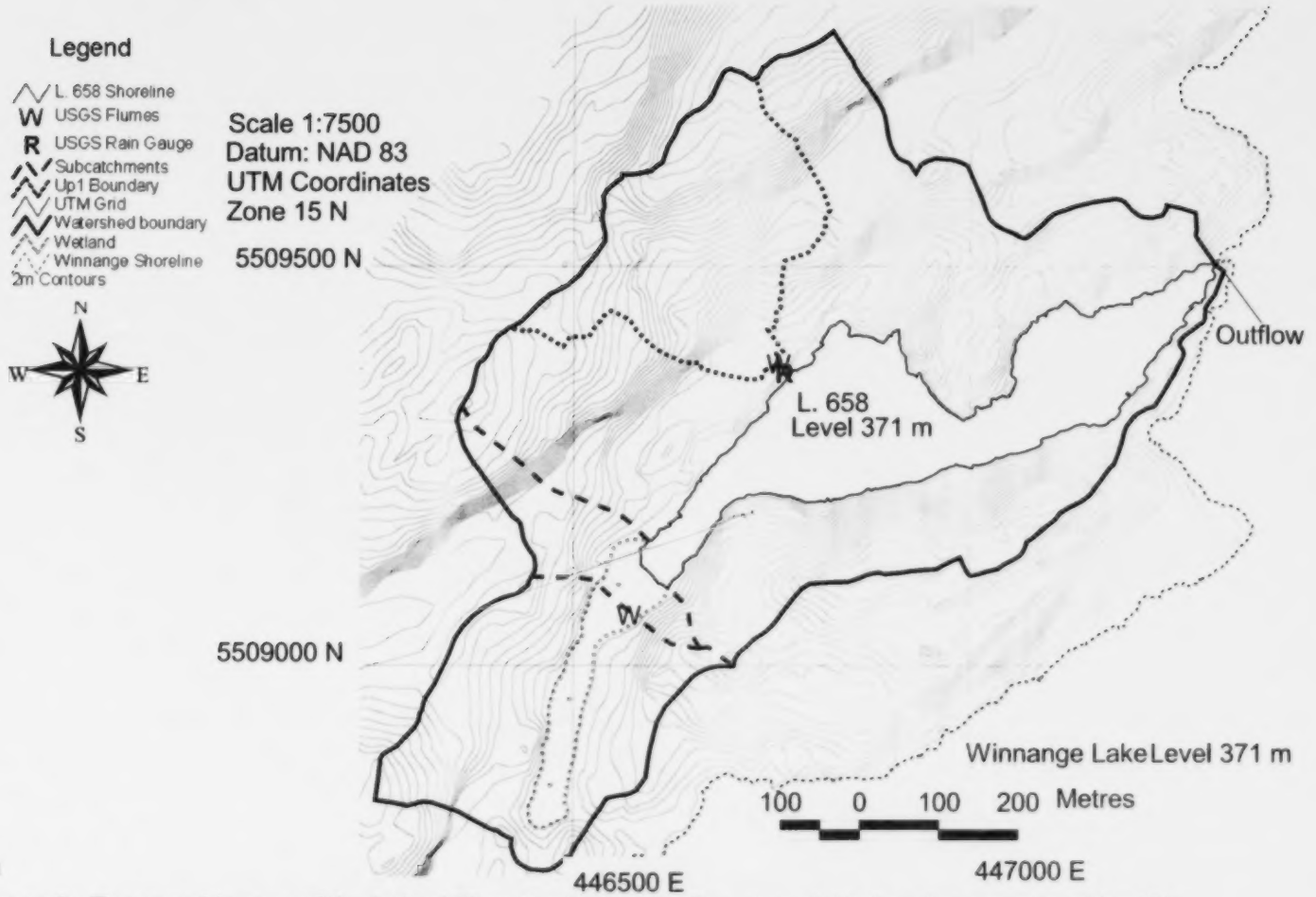

Figure 2. Topographic map of the Lake 658 watershed at the Experimental Lakes Area produced by Atlis Geomatics from 1982 aerial photography. Watershed boundaries determined from interpretation of contours and ground truthing. Contours are at two-metre intervals.

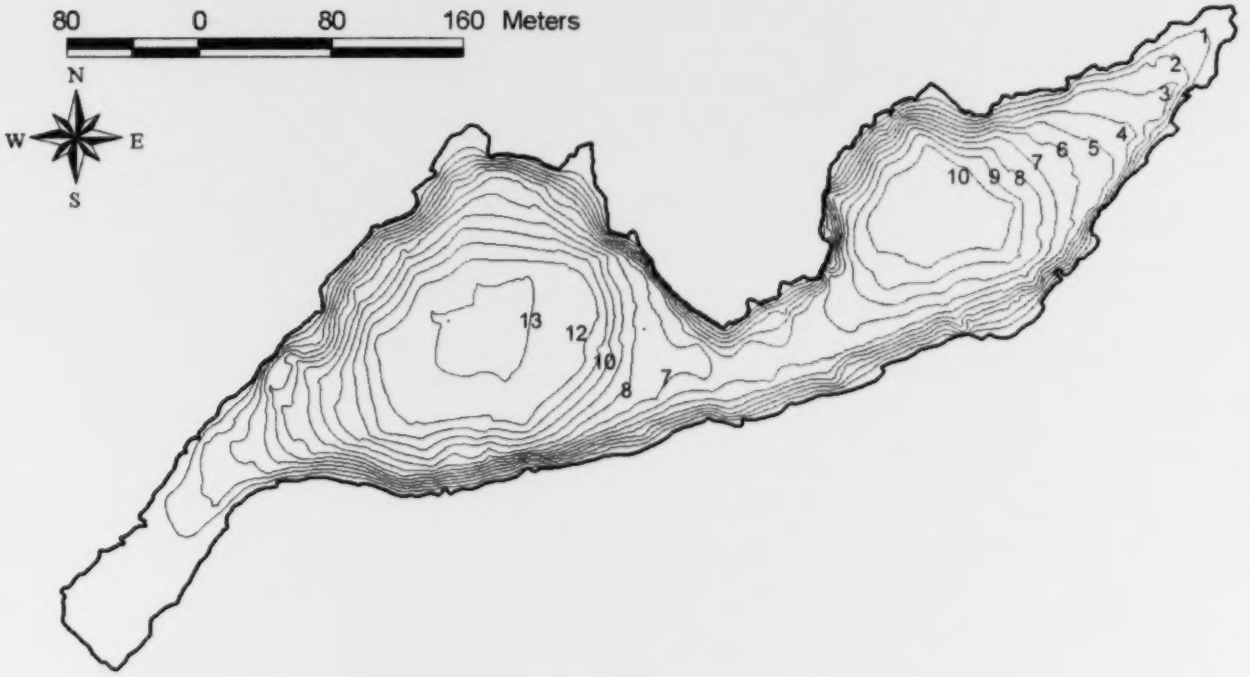

Figure 3. Bathymetry map for Lake 658. Bathymetry was surveyed on September 8, 2003. Lake level on the day of the survey was 8.90 m relative to an assumed datum. Depth data were collected using a SIMRAD EY500 hydroacoustic unit equipped with a split beam 120 kHz transducer. Contours were constructed using the TOPOGRID command in ArcInfo (ESRI, Redlands, Calif.), which employs an interactive finite difference interpolation technique (Hutchinson, 1988 and 1989).

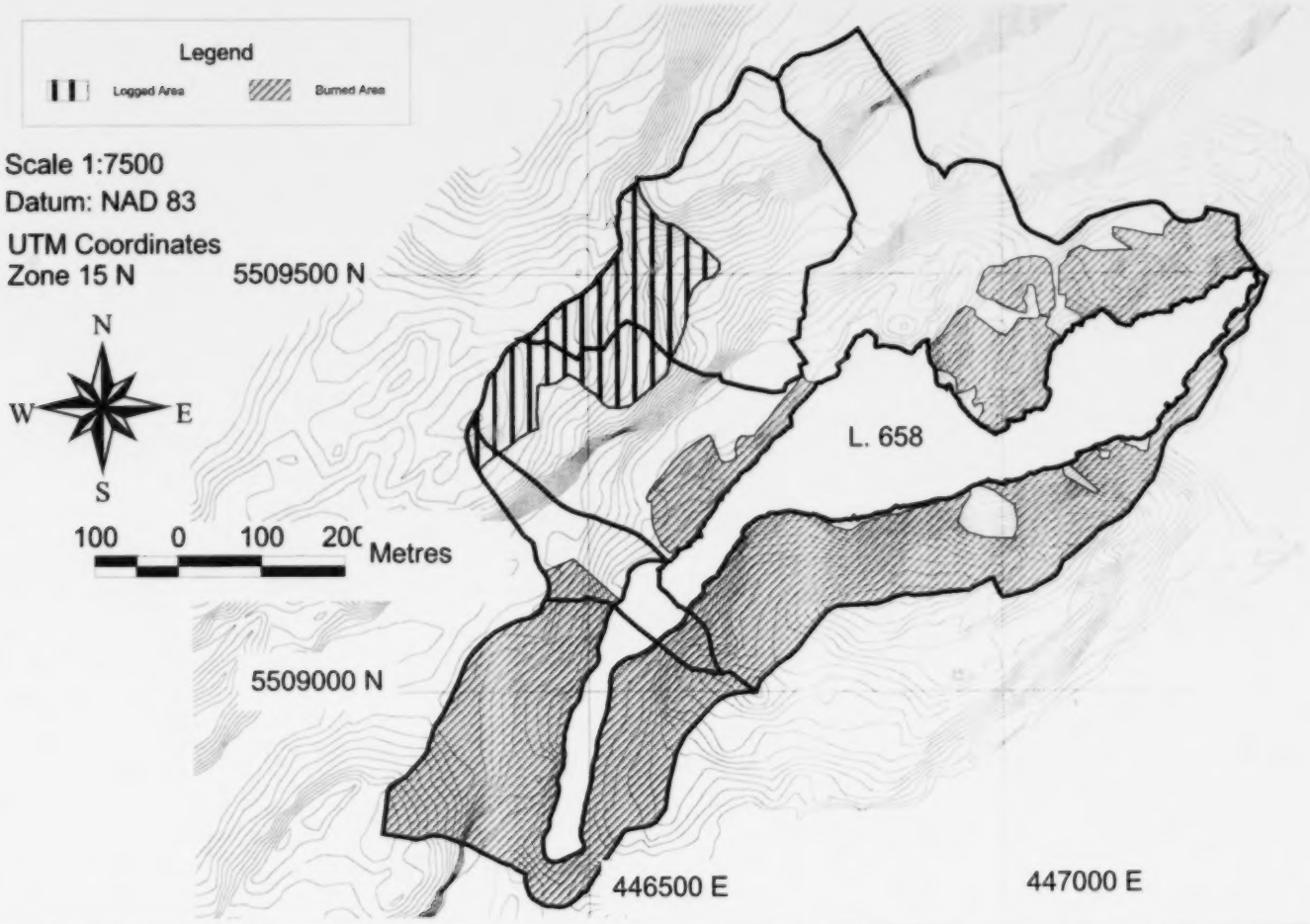

Figure 4. Map of the Lake 658 wathershed showing areas logged (~1978), and burned (fall of 1983). The logged areas are delimited from the1982 aerial photos. The burned areas are delimited from colour aerial photos taken August 2004.

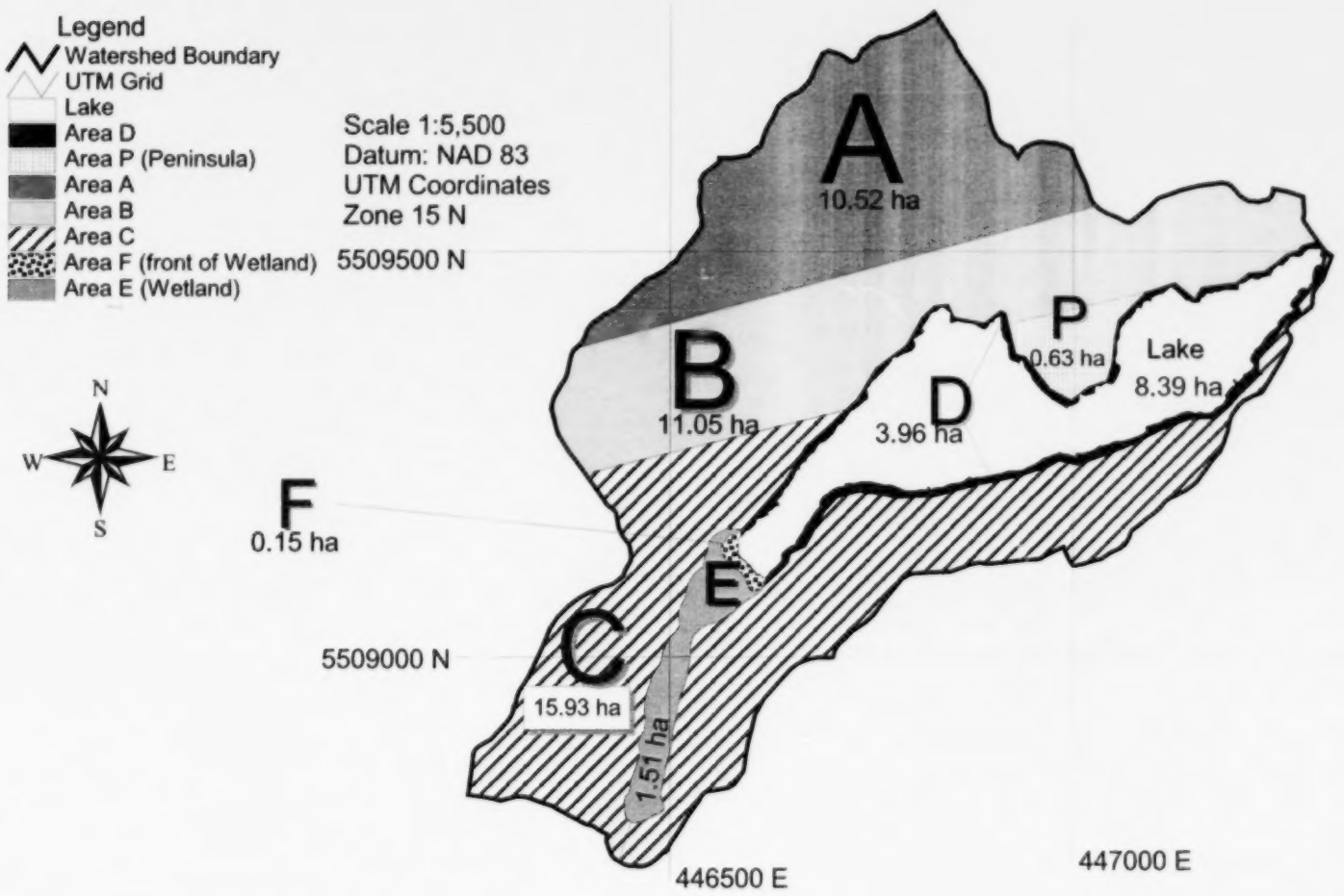

Figure 5. Terrestrial sprayblock outlines and areas of the Lake 658 watereshed.
note: Area D is not drawn to scale.

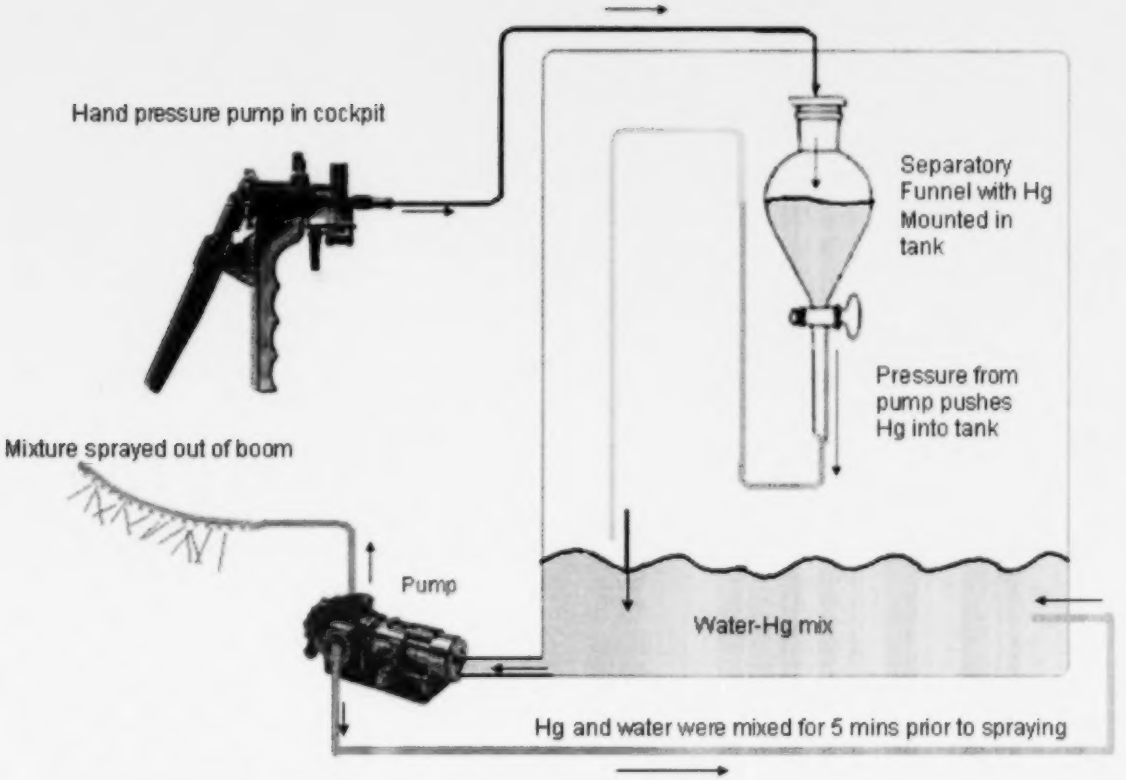
Hand pressure pump in cockpit
Separatory Funnel with Hg Mounted in tank
Pressure from pump pushes Hg into tank
Mixture sprayed out of boom
Pump
Water-Hg mix
Hg and water were mixed for 5 mins prior to spraying

Figure 6. Diagram of the mixing apparatus in the aircraft.

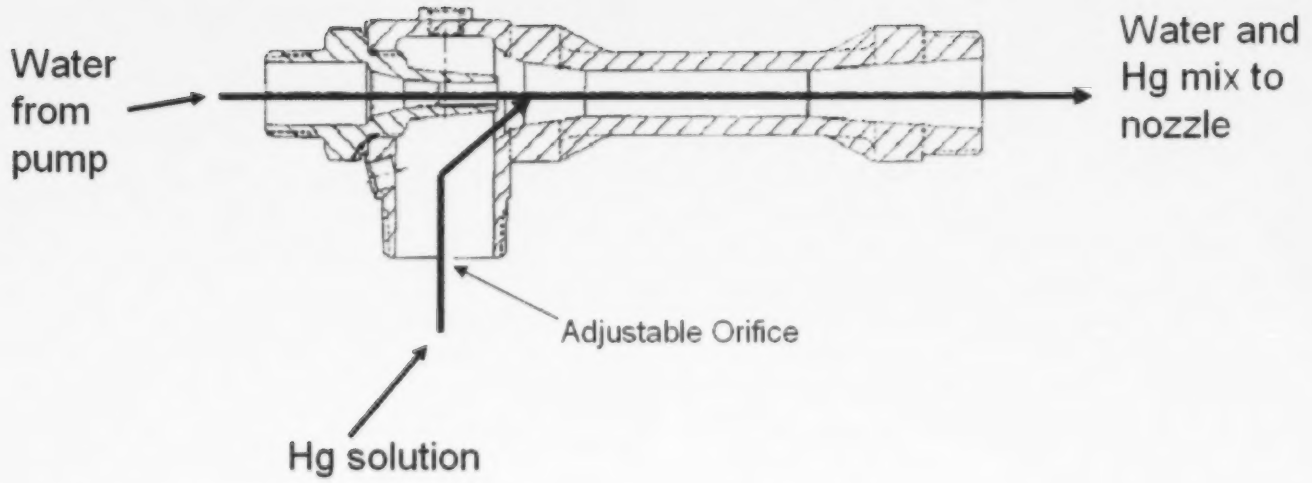

Figure 7. Diagram of eductor apparatus used in shoreline spraying.

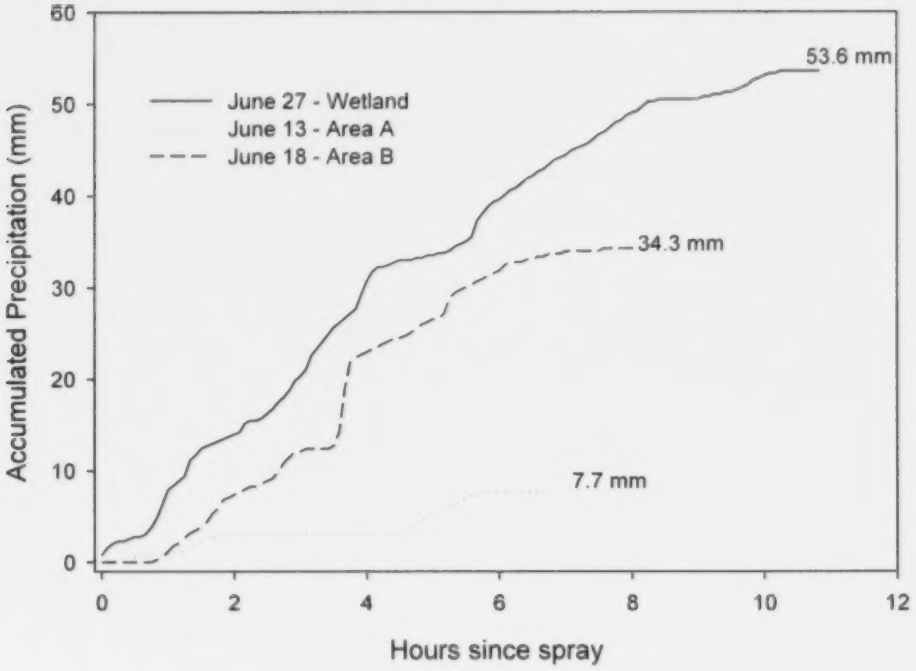

Figure 8. Accumulated precipitation after each spray event in 2001, showing total amounts. Data from USGS open rain gauge located at Lake 658.

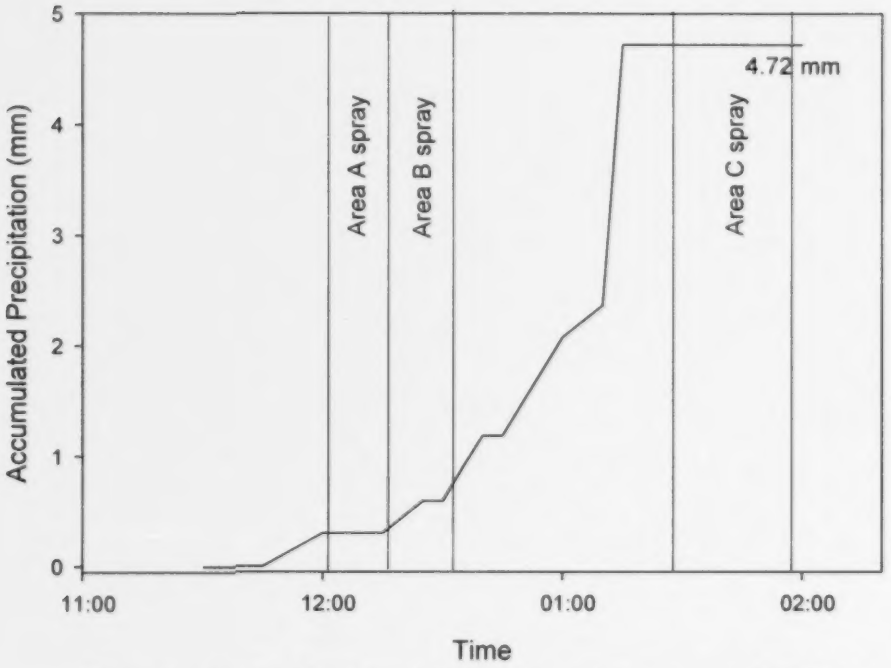

Figure 9. Accumulated precipitation for each spray event in 2002 showing spray events and total precipitation amount. Data from USGS open rain gauge located at Lake 658.

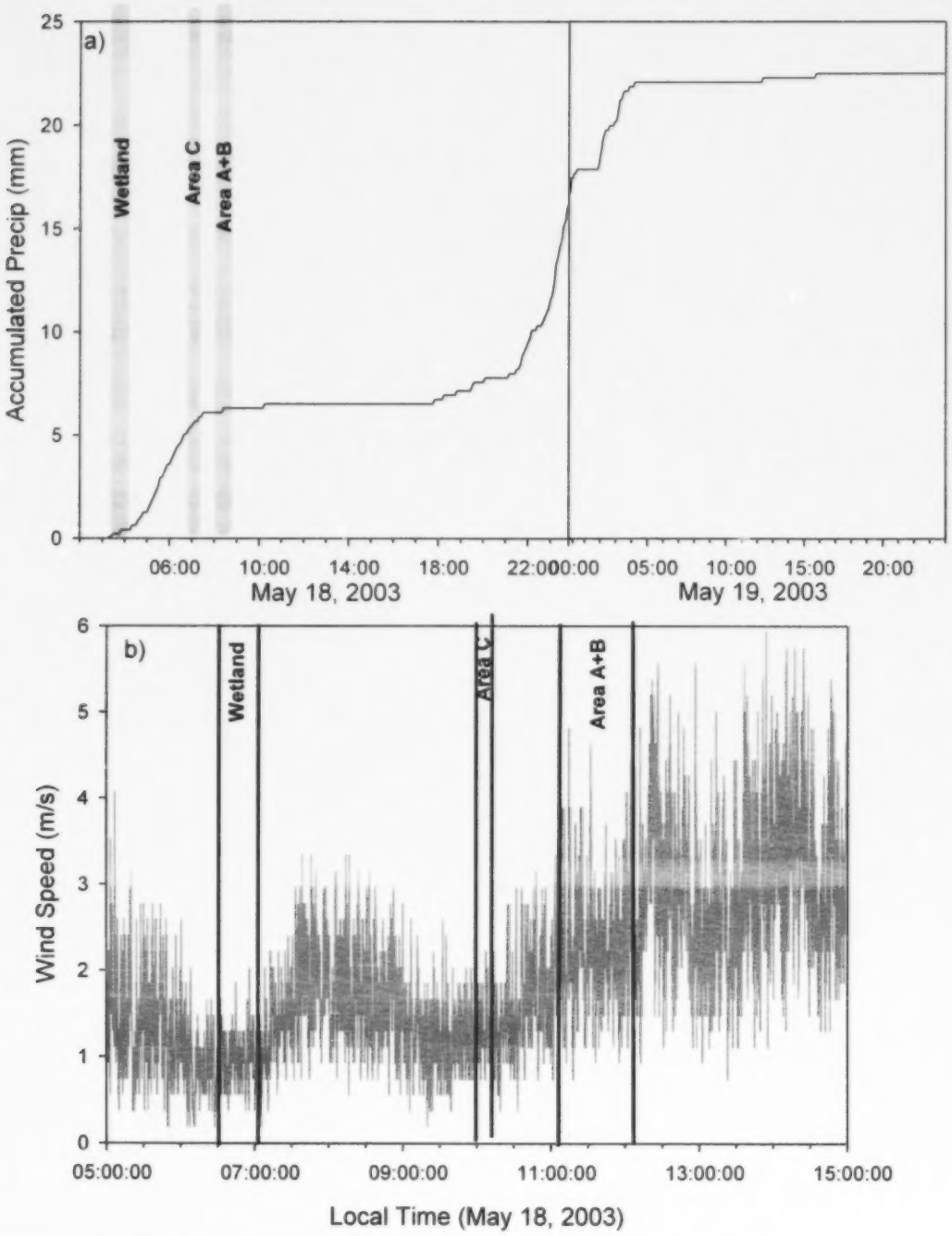

Figure 10. Accumulated precipitation (a, USGS open rain gauge at Lake 658) and wind speed (b, North side weather station) for each spray event in 2003.

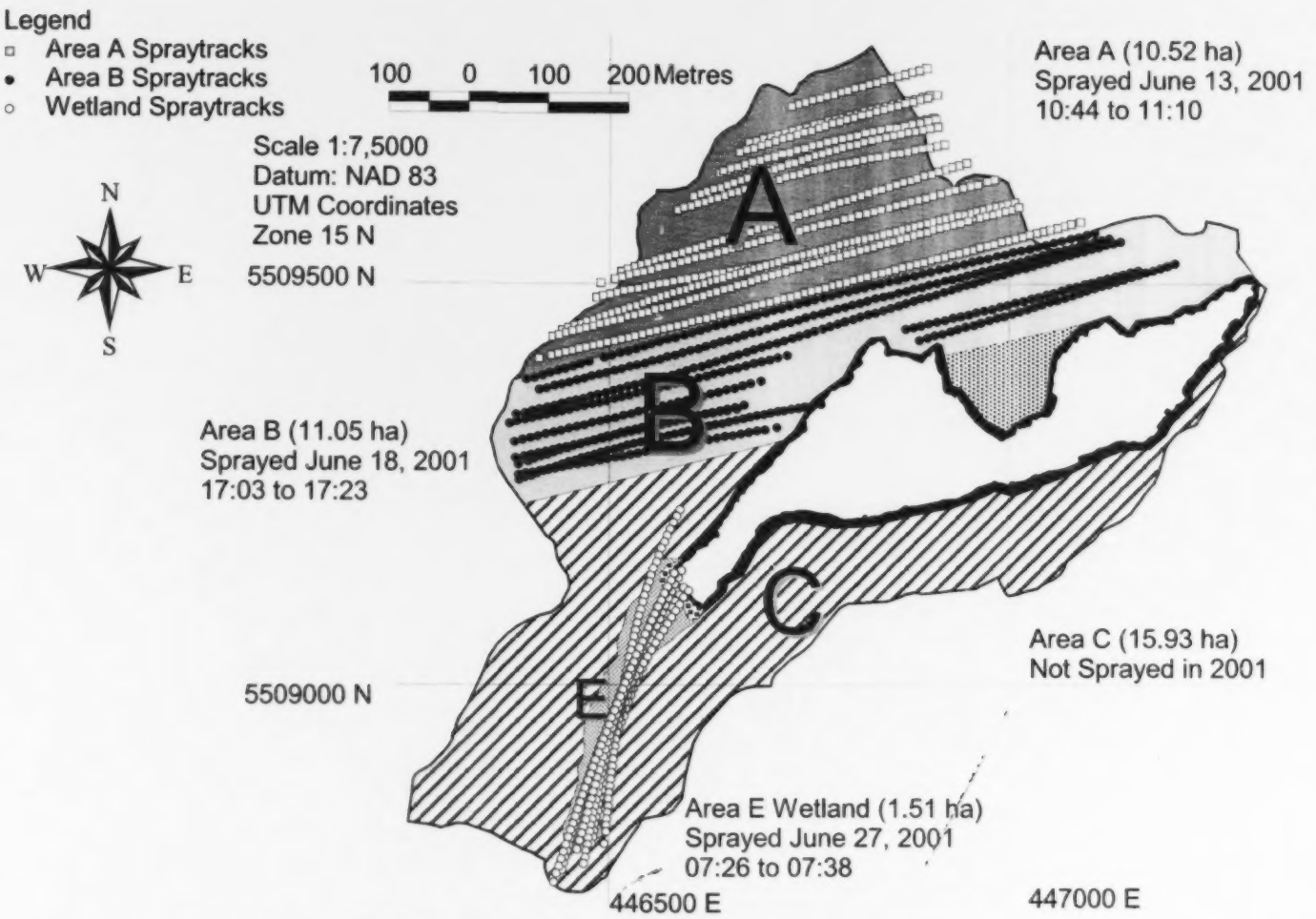

Figure 11. Aerial Spray tracks in 2001. Data from aircraft's GPS unit during spraying.

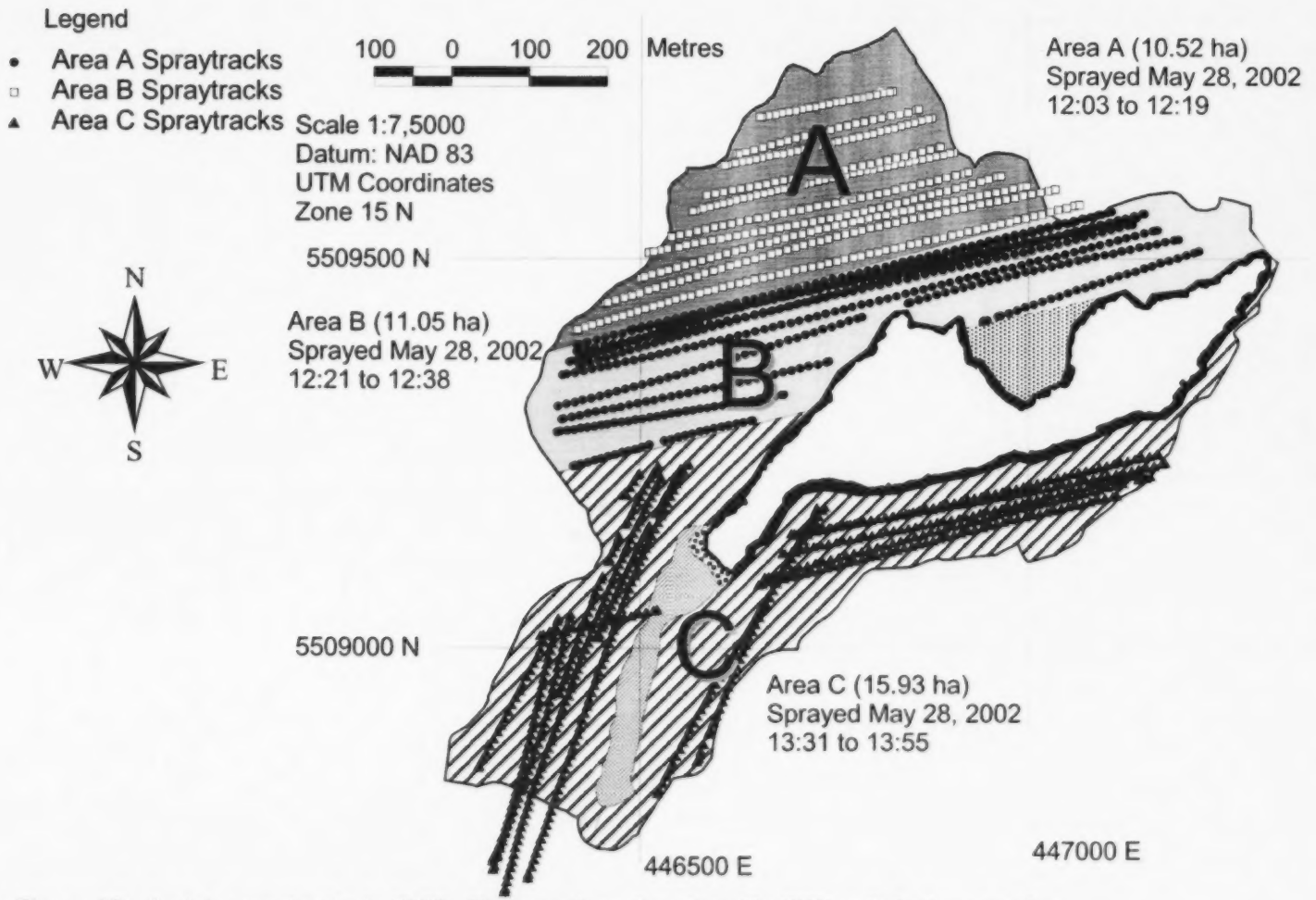

Figure 12. Aerial spray tracks in 2002. Data are from the aircraft's GPS unit during spraying.

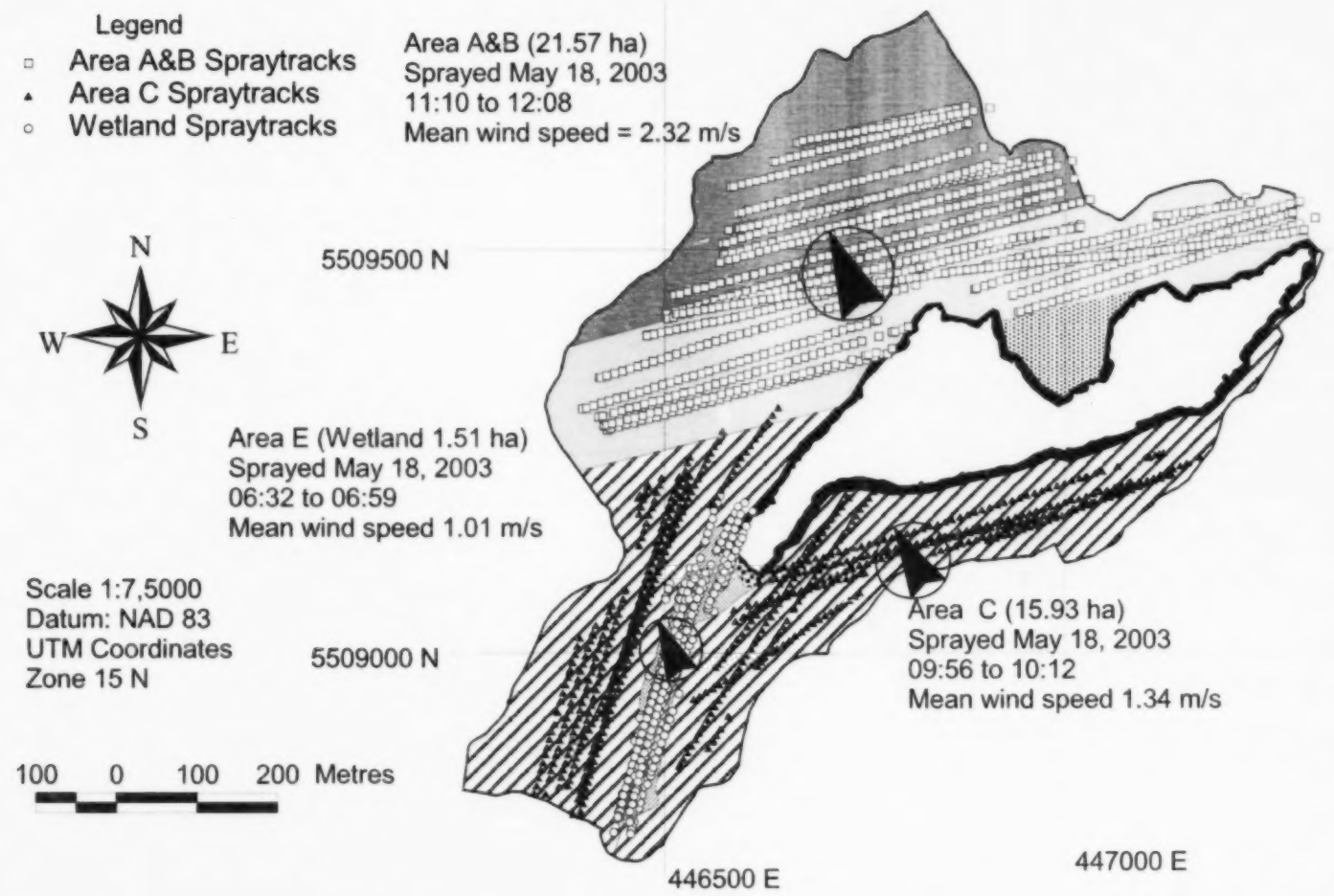

Figure 13. Aerial spray tracks in 2003. Spraytracks are data from aircraft's GPS unit during spraying. Arrows show the direction of wind during spraying.

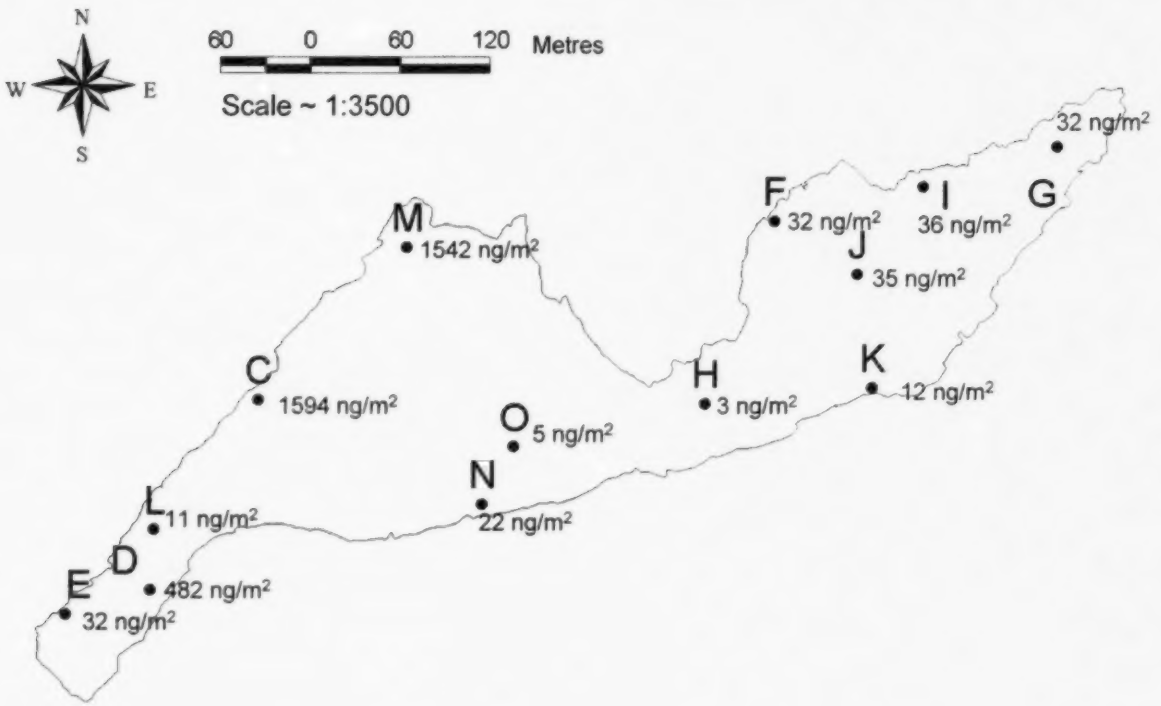

Figure 14. Location of overspray collectors on Lake 658 in 2002. Numbers at each location are the amounts of Upland Spike Hg deposition at that collector.

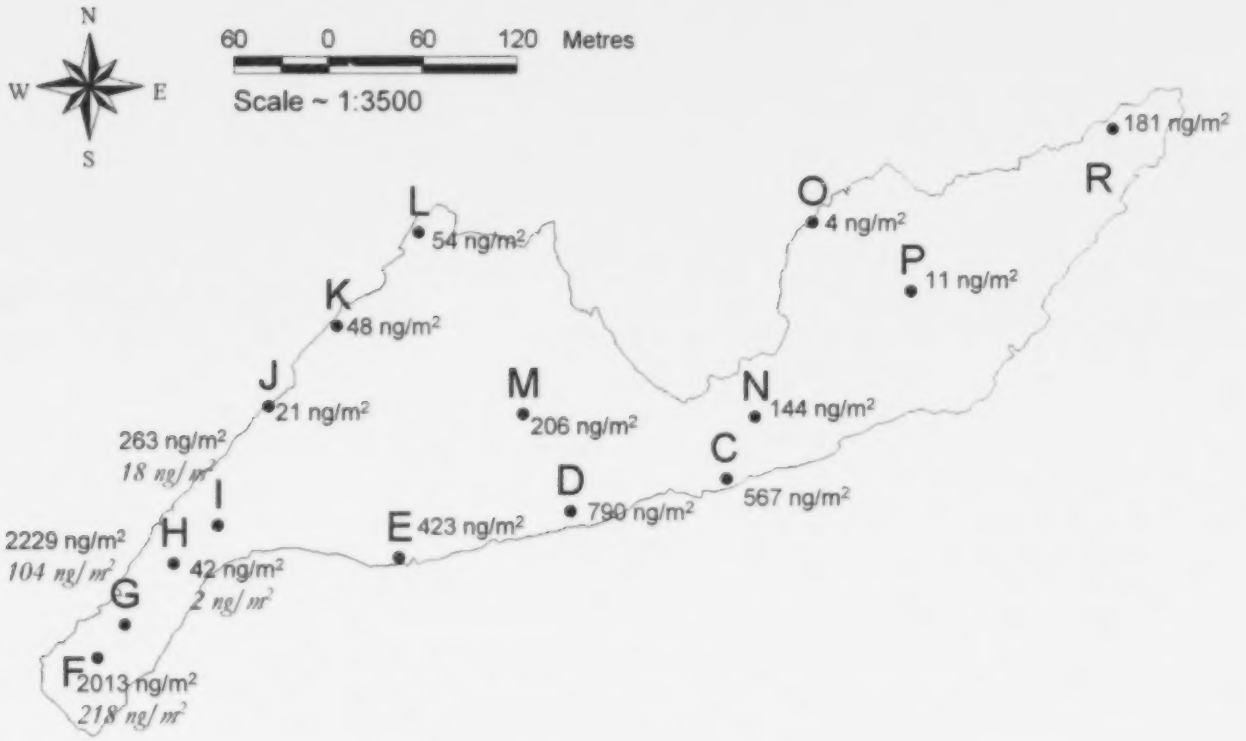

Figure 15. Location of overspray collectors at Lake 658 in 2003. Numbers at each location are the amounts of deposition of Upland Spike Hg, and Wetland Spike Hg (in italics) at that collector.

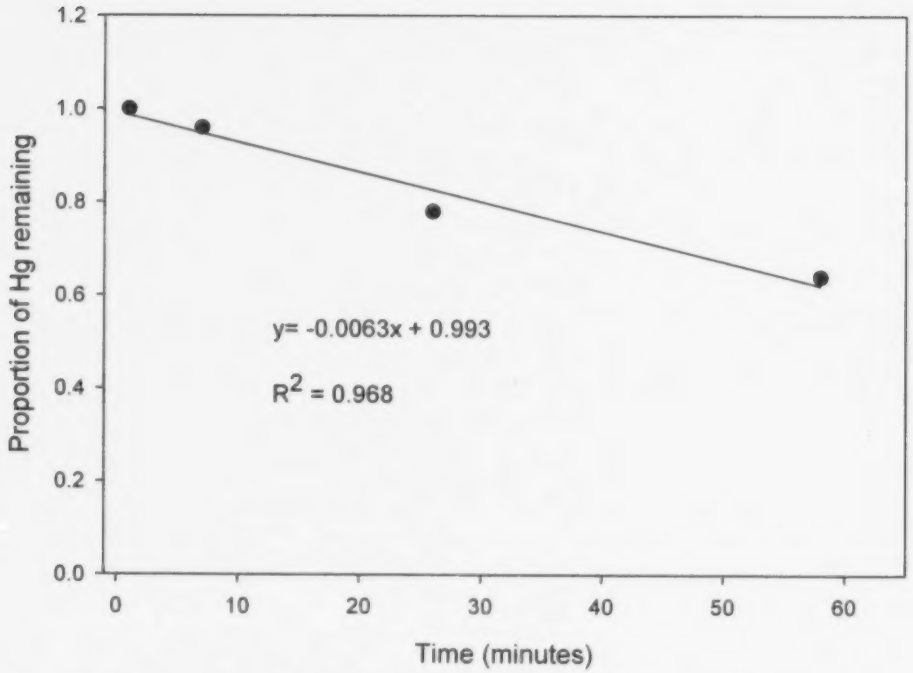

Figure 16. Test of Hg loss in spray plane and pump system under actual spray conditions (plane was actually flying between sample collection).

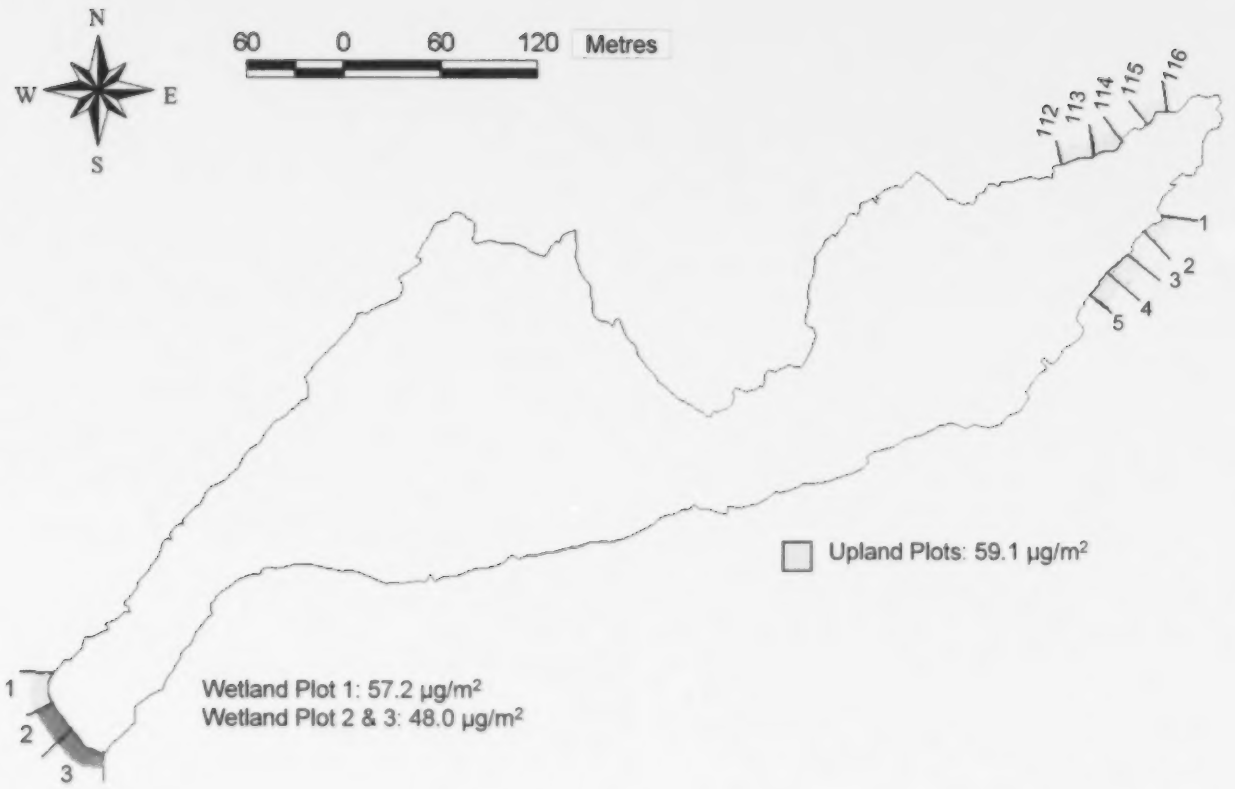

Figure 17. Shoreline areas sprayed in 2002 and application rates.

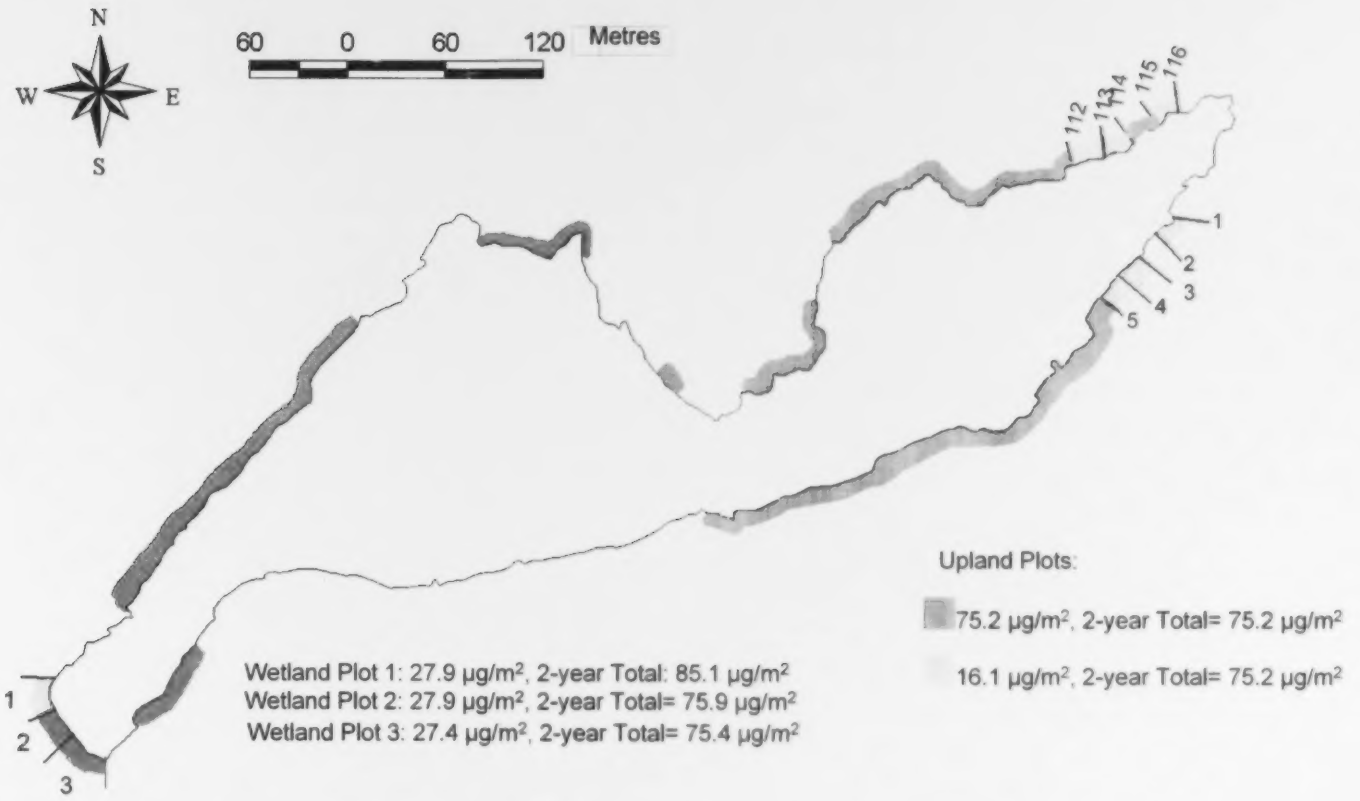

Figure 18. Shoreline areas sprayed in 2003 and application rates for 2003 and two–year totals.